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TENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1902.

BY F. W. CLARKE.

Received October 16, 1902.

DURING 1902 there has been a fair amount of activity in the determination of atomic weights, and some of the work published is highly important. One new metal, radium, appears as a definite element for the first time, taking its proper place in the periodic system as a member of the calcium, strontium, barium group. The recorded investigations are summarized below. The work on iodine, calcium, selenium, lanthanum, and uranium is especially worthy of notice.

IODINE.

In order to establish more exactly the relative positions of tellurium and iodine under the periodic law, Ladenburg[1] has redetermined the atomic weight of the latter element. His process consisted in transforming silver iodide to silver chloride, by heating in chlorine, and a preliminary series of experiments gave the following results. All weights were reduced to a vacuum, and the calculations are based upon O = 16.

[1] *Ber. d. chem. Grs.*, **35**, 2275.

Weight AgI.	Weight AgCl.	Atomic weight I.
31.2558	19.0817	126.93
33.7357	20.5930	126.96
49.88229	30.4525	126.94
47.8830	29.2262	126 98
60.1435	36.7154	126.95
41.3649	25.2448	127.01
50.8916	31.0664	126.95
41.3233	25.2200	126.98
80.8139	49.3181	127.02
89.5071	54.6367	126.96
		Mean, 126.97

This value is notably higher than that given by Stas, 126.85, and therefore additional determinations were necessary. Three experiments, conducted with the utmost care and with all needful precautions, gave as follows:

Weight AgI.	Weight AgCl.	Atomic weight I.
62.6608	38.2496	126.957
63.8351	38.9656	126.961
74.7516	45.6288	126.963
		Mean, 126.960

This result serves to vindicate the preliminary series, but the cause of the difference from Stas' value is yet to seek. One careful experiment by Stas' method, the synthesis of silver iodide, was made by Ladenburg, whose data, with all corrections applied, are these:

50.3147 Ag gave 109.4608 AgI. Hence I = 126.87.

Here Stas is corroborated, and the difference is evidently due to the different methods. Ladenburg regards the synthesis of the iodide from silver as attended by much greater errors than affect the other method, and says that their tendency is to lower the apparent atomic weight of iodine. The new data, therefore, are entitled to very respectful consideration.

Two syntheses of silver iodide are also given by Scott,[1] incidentally to his research upon tellurium. The data are subjoined, and represent reductions to a vacuum, and calculations based upon O = 16 and Ag = 107.93.

Weight Ag.	Weight AgI.	Atomic weight I.
4.6240	10.0634	126.96
6.39978	13.92913	126.98

[1] *Proc. Chem. Soc.* (London), **18**, 112, May 7, 1902.

Here again there is a variation from Stas, and an agreement with the higher value obtained by Ladenburg. It seems clear that the atomic weight of iodine should be most carefully scrutinized.

CALCIUM.

An important preliminary notice by Richards[1] describes a number of experiments upon the atomic weight of calcium. The compound studied was the chloride, and the results, reduced to a vacuum, were as follows: (O = 16, Cl = 35.455.)

Weight $CaCl_2$.	Weight AgCl.	Atomic weight.
1.56454	4.0409	40.121
3.57630	9.2361	40.130
3.59281	9.2788	40.129
5.00880	12.9364	40.124
9.00246	23.2506	40.125
	Mean,	40.126

Still another paper upon this subject, by Hinrichsen,[2] is supplementary to the memoir which he published in 1901.[3] Transparent calcite from Russia was reduced to lime by ignition. After reduction to a vacuum and correction for known impurities in the original material, the subjoined data were obtained.

Weight $CaCO_3$.	Weight CaO.	Atomic weight.
31.20762	17.49526	40.139
22.00588	12.33642	40.136

The value found in 1901 was Ca = 40.142. These figures harmonize with those of Richards, and prove that the formerly accepted number, Ca = 40, is too low.

SELENIUM.

Atomic weight redetermined by Julius Meyer.[4] Silver selenite, scrupulously pure, was analyzed electrolytically. The data, with all weights reduced to a vacuum, are as follows:

Weight Ag_2SeO_3.	Weight Ag.	Per cent. Ag.	Atomic weight.
0.5152	0.3241	62.907	79.28
0.5237	0.3295	62.915	79.24
1.8793	1.1826	62.928	79.17
2.1460	1.3503	62.922	79.20
1.6964	1.0672	62.910	79.27
		Mean,	79.23

[1] This Journal, **24**, 374.
[2] *Ztschr. phys. Chem.*, **40**, 746.
[3] *Ibid.*, **39**, 311.
[4] *Ztschr. anorg. Chem.*, **31**, 391; *Ber. d. chem. Ges.*, **35**, 1591.

From the sum of the weights, corrected for a trace of silver which remained in solution after electrolysis, the final result becomes

$$Se = 79.21.$$

This figure is nearly in accord with Lenher's determination, but notably higher than that obtained by Pettersson and Ekman.

TELLURIUM.

Guthier,[1] in order to determine the atomic weight of tellurium, has studied telluric acid and tellurium dioxide. His analyses depended upon the precipitation of tellurium by hydrazine hydrate, and special precautions were taken to avoid any oxidation of the precipitated metal. The latter was found to be extremely oxidizable. First, two direct determinations were made of water in telluric acid, as follows:

Weight H_6TeO_6.	Weight H_2O.	Per cent. H_2O.	Atomic weight.
0.4937	0.1162	23.54	127.60
0.9910	0.2335	23.56	127.70
		Mean,	127.65

All weights were reduced to a vacuum, and calculations were based upon $O = 16$ and $H = 1.008$.

Secondly, Guthier gives six determinations of tellurium in telluric acid, after several fractional crystallizations of the latter. Three separate fractions were studied, with duplicate determinations on each. The data are given below:

Weight H_6TeO_6.	Weight Te.	Per cent. Te.	Atomic weight.
0.9380	0.5204	55.48	127.20
0.4963	0.2754	55.49	127.25
1.0485	0.5829	55.60	127.80
0.8865	0.4915	55.44	127.00
0.4339	0.2411	55.56	127.60
0.3492	0.1937	55.48	127.34
		Mean,	127.365

From tellurium dioxide, similarly reduced, the following data were obtained.

Weight TeO_2.	Weight Te.	Per cent. Te.	Atomic weight.
0.1662	0.13287	79.94	127.50
0.3136	0.2507	79.94	127.50
0.2799	0.2238	79.95	127.60
		Mean,	127.53

[1] *Ann. Chem.* (Liebig), **320**, 52.

The average of the three series of determinations is

$$Te = 127.51.$$

The low results of the second series are probably ascribable to traces of mother-liquor retained in some crystals of the telluric acid.

A preliminary notice upon the atomic weight of tellurium has also been published by Scott.[1] The substances studied were trimethyl tellurium iodide, $Te(CH_3)_3I$, and the corresponding bromide. Analyses of the iodide were as follows:

Weight $Te(CH_3)_3I$.	Weight AgI.	Atomic weight.
1.7461	1.3688	127.70
6.6425	5.20575	127.66
8.0628	6.3181	127.69

The bromide was titrated with silver solution, and gave these results:

Weight $Te(CH_3)_3Br$.	Weight Ag.	Atomic weight.
2.4294	1.0373	127.77
6.8424	2.9201	127.78

The second sample of bromide was not so pure as the first. Rejecting it, the mean of the other four determinations gives $Te = 127.70$. The mean of all five is 127.74. All weights are reduced to a vacuum, and the antecedent values are $O = 16$, $C = 12.00$, $H = 1.0075$, $I = 126.85$, $Br = 79.95$, $Ag = 107.93$.

LANTHANUM.

The determinations of atomic weight by Jones[2] were made upon material of remarkable purity. The only contamination which could be detected with the Rowland spectroscope of the Johns Hopkins University, was a trace of cerium, amounting to not more than 0.01 per cent. and probably much less. Furthermore, some of the lanthanum oxide was ignited in hydrogen in order to make sure that no oxide higher than La_2O_3 was present. The method of determination was the usual synthesis of sulphate from oxide, and careful experiments showed that under the conditions of the investigation no acid sulphate was formed. The sulphate which was finally weighed was perfectly soluble in water and absolutely neutral in reaction. Twelve determinations are given, as follows: The atomic weight was calculated with $O = 16$, and $S = 32.06$.

[1] *Proc. Chem. Soc.* (London), **18**, 112, May 7, 1902.

[2] *Am. Chem J.*, **28**, 23.

Weight La_2O_3.	Weight $La_2(SO_4)_3$.	Atomic weight.
1.0122	1.7592	138.72
1.1268	1.9581	138.78
0.94585	1.6437	138.77
1.0675	1.8553	138.73
0.9030	1.5692	138.78
1.1273	1.9589	138.79
0.9407	1.6347	138.78
1.0455	1.8168	138.78
1.1271	1.9586	138.78
1.3074	2.2720	138.77
1.3389	2.3267	138.77
1.2012	2.0874	138.78
	Mean,	138.77

An attempt was also made to use the oxalate method, but that proved to be unsatisfactory.

A second memoir upon lanthanum, by Brauner and Pavlicek,[1] is even more elaborate than that of Jones. The method of determination was the same in both cases, but there are many differences of detail. The Bohemian authors find a serious difficulty in the presence of the acid sulphate, for which measured corrections are applied, and they also note another source of error in the hygroscopic character of $La_2(SO_4)_3$. The latter error was guarded against by special precautions in weighing. The final results (omitting a preliminary series), with vacuum weights, and all corrections applied, are as follows: The calculations depend upon $O = 16$ and $S = 32.06$.

Weight La_2O_3.	Weight $La_2(SO_4)_3$.	Atomic weight.
1.06562	1.85054	139.036
1.00694	1.74856	139.053
1.12553	1.95457	139.038
1.70276	2.95707	139.026
1.02460	1.77943	139.009
1.28650	2.23419	139.024
1.06488	1.84910	139.068
	Mean,	139.036

The reverse method of determination, the ignition of sulphate to oxide, gave bad results. A series of determinations by the oxalate method gave in mean, $La = 139.07$, but the individual measurements show a wide range of variation, namely, from 138.67 to 139.66. The value for the atomic weight of lanthanum derived

[1] *J. Chem. Soc.*, **81**, 1243.

from the sulphate syntheses is doubtless not far from the truth. The mean of the Jones and Brauner values is

$$La = 139.905,$$

and, pending further evidence, this value may properly be adopted; although Brauner, in a later communication,[1] criticizes the work of Jones and argues in favor of his own determinations. Brauner insists strongly upon the presence of acid sulphate in the lanthanum sulphate studied by Jones, and also suggests that the latter overlooked the hygroscopic nature of his material. If further investigation sustains these criticisms, then the Brauner value is to be preferred.

YTTERBIUM.

Atomic weight redetermined by Astrid Cleve,[2] with very pure material. The method employed was the synthesis of the sulphate from the oxide. The data are as follows, when $O = 16$ and $S = 32.06$.

Weight Yb_2O_3.	Weight $Yb_2(SO_4)_3$.	Atomic weight.
0.7791	1.2535	173.22
0.5190	0.8353	173.05
0.4905	0.7894	173.07

These figures confirm the earlier determination by Nilson.

URANIUM.

The work of Richards and Merigold[3] upon the atomic weight of uranium is rich in details, and also in matter relative to probable sources of error. The substance finally chosen for study was uranous bromide prepared by sublimation, and scrupulously protected from the oxidizing action of the air. It contained a minute quantity of sodium bromide, but the amount of this was determined, and the necessary correction was applied. All weights refer to a vacuum, and the antecedent atomic weights were $O = 16$, $Ag = 107.93$, and $Br = 79.955$. A preliminary series of analyses gave as follows, all corrections included:

Weight UBr_4.	Weight AgBr.	Atomic weight.
2.2058	2.9699	238.36
1.4418	1.9401	238.69
1.4050	1.8910	238.56
1.1749	1.5818	238.39
	Mean,	238.50

[1] *Ztschr. anorg. Chem.*, **33**, 317.
[2] *Ibid.*, **32**, 129.
[3] *Proc. Amer. Acad.*, **37**, 365.

In another and final set of experiments, the uranous bromide was titrated with known amounts of pure silver, and the precipitated silver bromide was also weighed. Hence two ratios were determined, with the following results:

Weight UBr_4.	Weight AgBr.	Atomic weight.
1.7999	2.4226	238.54
1.0662	1.4352	238.50
1.8551	2.4967	238.59
	Mean,	238.54

Weight UBr_4.	Weight Ag.	Atomic weight.
1.7999	1.3918	238.49
1.0662	0.8245	238.46
1.8551	1.4342	238.60
	Mean,	238.52

Average of all determinations,	238.52
Average of last six determinations,	238.53

This result is notably lower than the usually accepted value for the atomic weight of uranium.

From series 2 and 3 the ratio between silver and bromine may be deduced. It gives for the percentage of Ag in AgBr the number 57.447. Stas found 57.445. This agreement is eminently satisfactory.

RADIUM.

By many fractional crystallizations, Madame Curie[1] has succeeded in preparing radium chloride sufficiently pure for determinations of the atomic weight of the metal. According to Demarçay, who examined the spectrum of the material, it contained a minimum quantity of barium, incapable of exerting any appreciable influence upon the atomic weight. Three analyses were made, the chlorine being weighed as silver chloride, with the following values deduced for the atomic weight of radium.

	225.3
	225.8
	224.0
Mean,	225.0

MISCELLANEOUS NOTES.

Several papers have appeared during the year, dealing with numerical relations between the atomic weights of the various

[1] *Compt. Rend.*, **135**, 161.

elements. Three of them, by Bilecki,[1] Marshall,[2] and Hollins,[3] relate to possible modifications of "Prout's law"; that is, they point out relations analogous to, but not identical with, those assumed by Prout. Schmidt[4] and Stoney[5] discuss the connection of the atomic weights in a more purely mathematical way, and so too does Vincent.[6] The logarithmic spiral of Stoney is especially suggestive. There is also an elaborate memoir by Lord Kelvin[7] on the "weights of atoms"; and a discussion by Clarke[8] of the best method for the reduction and combination of atomic weight determinations. Ebaugh's work on the atomic weight of arsenic,[9] which was cited in the report of your committee for 1901, has appeared in full in this Journal.

INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

This committee, which was too large for effective working, has appointed a smaller body for action. This smaller committee, consisting of F. W. Clarke, T. E. Thorpe and Karl Seubert, has already reported, and its report has appeared in this Journal.[10] The table of atomic weights, there given, need not be repeated here.

THE DISTRIBUTION OF HYDROGEN SULPHIDE TO LABORATORY CLASSES.

BY CHARLES LATHROP PARSONS.

Received December 2, 1902.

SO MUCH has been written regarding new forms of generators for hydrogen sulphide and their use in the laboratory that one must needs approach the subject with trepidation and, at least, the semblance of an apology. There are, however, few teachers of chemistry who have not experienced the many inconveniences in the use of this most important laboratory reagent, inconveniences that are too frequently little understood by the student himself and which are generally the direct result of wasteful use. It is

[1] *Chem. Ztg.*, **26**, 399.
[2] *Ibid.*, **26**, 663, and *Chem. News*, **86**, 88.
[3] *Chem. News*, **86**, 147.
[4] *Ztschr. anorg. Chem.*, **31**, 147.
[5] *Phil. Mag.* (6), **4**, 411 and 504.
[6] *Ibid.*, (6), **4**, 103.
[7] *Ibid.*, (6), **4**, 177 and 281.
[8] *Am. Chem. J.*, **27**, 321.
[9] This Journal, **24**, 489, June, 1902.
[10] V. **25**, p. 1, January, 1903; and *Ztschr. angew. Chem.*, **15**, 1305.

always easy to instruct students to allow the gas to flow through the solution undergoing analysis at a rate no faster than one or two bubbles a second and always to close the outlet when not in use, but it is an impossibility to attain this result with individuals. Also the constant cleaning and replenishing of the large generators and the limited efficiency which most of them possess has led many instructors to require each student to prepare his own hydrogen sulphide as wanted rather than to depend upon a general laboratory supply. This method is to be deplored even with small classes, while with larger numbers it leads to a laboratory condition which there is no necessity to describe. The constant use in my laboratories, for several years, of the main principle of the apparatus about to be described and the almost complete removal of the difficulties I had before experienced, emboldens me to become a contributor to this already voluminous subject.

THE SYSTEM OF SUPPLY.

The usual small lead pipe of approximately 8 mm. diameter is

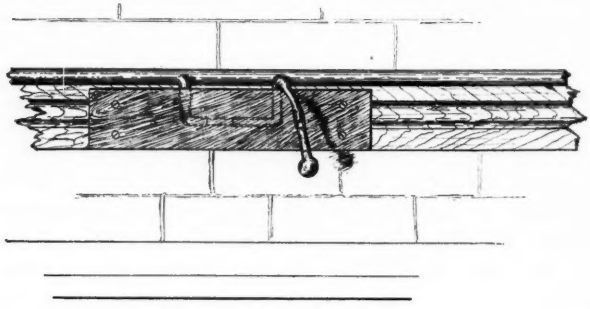


Fig. 1. Detail of outlet.

run from hood to hood where wanted and in each hood any number of short lengths of 4 mm. diameter are soldered on for outlets. The ends of these smaller outlets are then fused together and a fine opening made with a needle. To these lead outlets are attached, by means of a rubber connection, pieces of thermometer tubing bent as shown in Fig. 1 and of such a length that only a limited flow of gas can be obtained under the pressure used. In my own practice, under a pressure of 20 cm., a length of about 12 cm. is required to check the flow down to the rate of 2 bubbles a second which is fast enough for any ordinary use. The ther-

mometer tubing is bent as shown in the figure and another short piece of rubber tubing is attached for a final outlet. This is closed with a simple glass plug, which is much to be preferred to a clamp. The whole, with the exception of the end of the rubber tube carrying the plug, is hidden from sight by a wooden block appropriately channeled on the back to receive the thermometer and lead tubing, and screwed on. The student removes the plug, inserts his own delivery tube, secures a fixed flow of gas and, as the whole system is apparently open when he removes his delivery tube, he seldom fails to insert the plug. If he does, but little harm ensues. The flow can be regulated by the length of the thermometer tubing used and the length of tubing required can easily be determined by experiment. A few centimeters variation in pressure makes but little difference in the flow. The rubber tubing connections should be made tight and permanent by slightly heating the lead and glass and they need to be renewed about once each year. There is practically no trouble arising from the stoppage of the capillary tube, only some half dozen tubes having been stopped up in an experience of five years.

THE GENERATOR.

The generator (Fig. 2) consists of three essential parts: (1) The acid container *A*. (2) The trap and holder of spent acid *B*. (3) The iron sulphide holder and gas generator proper *C*. All of these parts may be made of glass, porcelain or heavily glazed earthenware. Earthenware is much the cheapest but I have experienced much difficulty in having it made gas-tight. This is fundamental in the construction of the tower and bell *C*. By coating a common earthenware tower with asphalt paint both inside and out I have, however, obtained excellent service from the one now in use.

The acid container *A* holds approximately 10 liters of acid. It is so arranged by means of an inverted jug, or bottle, that the level is maintained constant at *h*. The inverted bottle has a shoulder blown on which, resting on the top of the containing jar, holds it in place. It is filled with 1:8 sulphuric acid or 1:4 hydrochloric acid. The hydrochloric acid is quicker in its action on the iron sulphide and for that reason only is to be preferred. The sulphuric acid, however, is cheaper, answers every purpose and no trouble whatever is experienced from the sulphate formed. The pressure is determined by the perpendicular distance between *h*

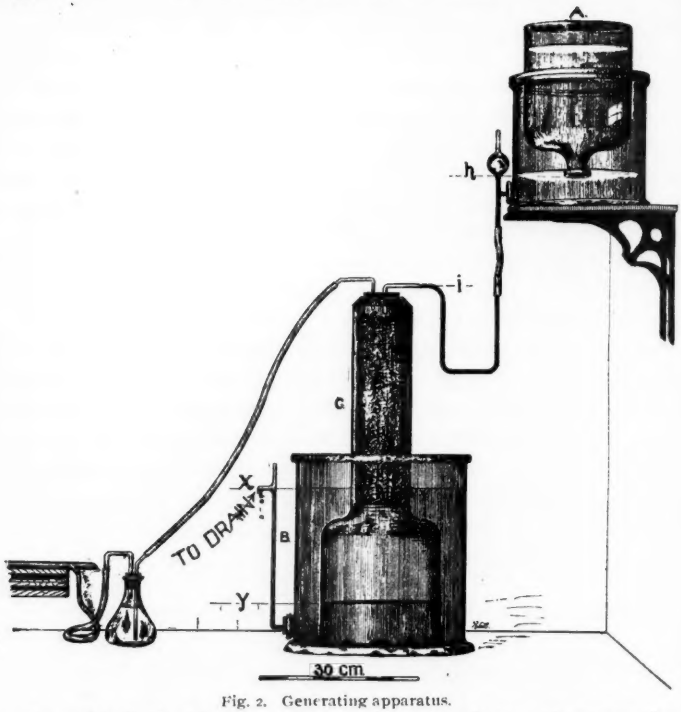


Fig. 2. Generating apparatus.

and i and is limited by the greatest adjustable distance between the equal and balancing pressure x and y. The connection between A and C is made by means of a U-shaped glass and rubber tube. It will be easily understood that any increase of pressure in C caused by the production of gas will immediately force the acid back into the arm nearest to C thus stopping the flow of acid. The variation due to this increase of pressure, while completely stopping the flow of acid, is seldom so great as a single centimeter, for the enlargement at the bottom of C takes up the excess of gas and the counterbalancing pressure x to y serves as a cushion. The entrance tube at the top of C should be about 1 cm. in diameter to avoid a slight siphon action which is caused by the short bend where it enters. The glass level outside of A serves simply to show when the acid supply in the inside container is exhausted, provided this is made of opaque material.

The holder B is 35 cm. high by 28 cm. inside diameter, and is

provided with a constant level and overflow to drain. It should be covered to prevent evaporation and consequent crystallization of sulphate. The rate of diffusion of a gas through a liquid is so slow that there is practically no odor thrown off into the room from the surface of the liquid.

The tower *C* is the gas generator proper and consists of a bell jar 22 by 25 cm. as a gas holder and pressure cushion, having a few openings at the base for the free passage of liquid. To the top of the bell jar is attached a cylinder 10 cm. inside diameter and 50 cm. high having four constrictions at the base to hold a perforated plate. It is filled with iron sulphide in small lumps or broken sticks. The bell jar and cylinder are best made in one piece, but if made of glass they may be connected by means of a ground joint. This presents no advantage from the standpoint of the chemist but does from that of the glass-blower. The acid enters the tower drop by drop and in trickling through, the iron sulphide is soon exhausted. Even with a large number of outlets in actual use the acid seldom enters other than dropwise. A small wad of glass wool should be placed on top of the iron sulphide to spread the acid and prevent the formation of channels. The exit tube should pass to a wash-bottle more for the purpose of making the rate of gas flow visible and of detecting any leak in the line when not in use than for any need of purification of the gas. It will also be apparent that when the generator is first placed in action the flow of the acid should be controlled by pressing the rubber tube with thumb and forefinger until the pressure between *x* and *y*, which balances that between *h* and *i*, has established itself.

A generator of this size will easily supply 100 outlets of the form described, even if all were in use at one time. A smaller generator is, however, not to be recommended in any case, for a considerable width and height of the iron sulphide column is essential to its proper working and to insure the almost complete neutralization of the acid. The generator can be easily shut off each night although this is never done in my own practice. A leak is at once made apparent by the gas wash-bottle and easily found with a piece of lead acetate paper.

The following advantages are claimed for this form of generator. They include all of those mentioned by Richards as desir-

able in his very complete article on the subject of gas generators.[1]

(1) Like the Kipp generator it is perfectly automatic so long as the gas flow is choked to less than the maximum capacity of the generator.

(2) The pressure is regulated at will and is almost constant for the height chosen. In practice it seldom varies by so much as a single centimeter.

(3) Only fresh acid comes in contact with the reacting solid.

(4) Under any normal requirements, the full capacity of the acid is obtained.

(5) The products of the reaction are automatically removed. Ferrous sulphate has never, in my experience, crystallized out in the bottom of the apparatus. Some small grains of ferrous sulphate do form in time on the iron sulphide itself but cause no trouble and can easily be removed by running a stream of water through the acid inlet for a few minutes. So far, I have never found this necessary, but it is easily accomplished and may well be done whenever the iron sulphide is renewed. Large crystals do not form.

(6) There are no stop-cocks or valves.

(7) It is easily cleaned and refilled without being taken down, simply by removing a rubber stopper.

(8) When used in connection with the economical choked supply system before outlined, it requires no attention whatever for days or even weeks at a time, depending wholly upon the amount of gas used, and then only to renew the acid, as the iron sulphide will outlast many acid supplies.

(9) If for any reason a large leak develops, the acid runs through rapidly, little iron sulphide is used up, and once the supply of acid has run through all action ceases. Of course, it does not distinguish between a small leak and a legitimate outlet.

The generator works equally well for the production and supply of carbon dioxide, the automatic action being sharper on account of the much more rapid evolution of gas. It is perhaps unnecessary to add that it may be used for the production of hydrogen or for any gas that is set free with a fair degree of rapidity, by the action of a liquid upon a solid.

NEW HAMPSHIRE COLLEGE,
DURHAM, N. H.

[1] *Am. Chem. J.*, **20**, 189.

A PLATINUM CRUCIBLE FOR CARBON COMBUSTIONS.

By John V. R. Stehman.

Received December 13, 1902.

Shimer[1] has shown that a platinum crucible provided with a special water-cooled stopper and rubber gasket, may be used as successfully as the more expensive platinum tube and gas-consuming furnace for carbon combustions.

The prevalent idea regarding his form of apparatus, seems to be a fear of the rubber gasket causing error by burning directly or by becoming hard and brittle, allowing small pieces to drop into the crucible, when the stopper is pushed into place.

In the following form of apparatus designed by the writer, no rubber gasket or washer is used, and, as in Shimer's apparatus, in place of the furnace, a Bunsen burner or blast-lamp is used, and air in place of oxygen.

It consists, as seen in the drawing, of three parts, *A*, *B* and *C*, also an asbestos washer, *d*. *A* is a water-cooled brass cup. *B* is the cup casing or crucible support, also made of brass. Part *C* is the platinum crucible, provided with a flange around the top, and was remodeled from a 30 cc. crucible. This special shape increases its length and allows over 1 inch to be brought to a full red heat when placed over the burner.

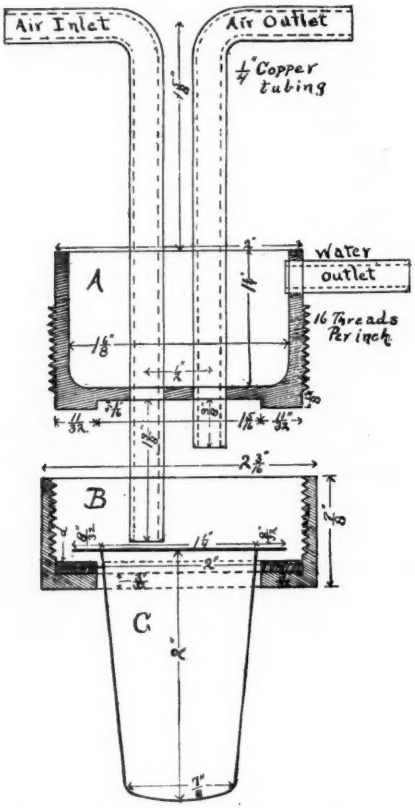
Part *d* is an acid-washed asbestos washer, made from a piece of asbestos wick yarn, of such a length as to allow the beveled ends to lap for about one-half inch. It is moistened and laid in place on the flange of casing *B*, then pressed into place by screwing cup *A* down upon it, the crucible being left out of place. This will force out the excess of moisture in the washer and flatten it. When the washer presents an even surface and has filled the flange of *B* full, it is ready to receive the crucible.

The crucible is now dropped into place, its flange resting upon the washer, and the cup *A* screwed down, using a gentle but firm pressure. That part of the cup *A*, which rests partly upon the flange of the crucible and partly upon the asbestos washer, is turned true, and polished, and coming in contact with the crucible flange and moist asbestos washer insures an air-tight joint. If water is now allowed to circulate through the cup at about 120 cc.

[1] This Journal, **21**, 557.

per minute the washer will remain moist when the crucible is heated with the blast-lamp, the casing and cup being protected by the asbestos board.

Two washers may be used, one above and one below the crucible



flange, or the flange of the crucible may rest directly upon the casing flange and the washer placed on top of the crucible flange. The author has used a pure rubber washer, letting it rest directly upon the flange of the crucible, which in turn rested upon the casing flange of *B*, but it was found that the blank determinations were always high, that is 0.0008 gram, but were constant, if care

was taken not to heat the crucible for more than about five-eighths of an inch from the bottom, to a red heat.

Once in place it is not necessary to remove the crucible, and a large number of determinations can be made, requiring no removal of the crucible, or rearrangement of the washer.

The cup *A*, it will be seen, carries an outlet and an inlet tube for air, brazed into place. It is also provided with an outlet tube for water, and by connecting this tube to a glass tube, giving to the water sufficient fall, it will act as a siphon and carry the water away rapidly. The inflow is obtained by allowing a glass tube attached to some source of supply, preferably the tap, to rest directly upon the bottom of the cup, and having the supply so regulated that the outflow will carry it off.

The train for the combustion of carbon as used with this apparatus consists of the following parts:

(1) Air supply obtained from furnace blast or aspirated from bottles.

(2) Potassium hydroxide bulbs containing potassium hydroxide of 1.40 sp. gr.

(3) A small guard tube to catch any drops of potassium hydroxide that might find their way from the potash bulbs.

(4) Combustion crucible, closed by a special water-cooled cup and casing and resting upon an asbestos board. The bottom part of the crucible projects 1¼ inches through the board and is heated by a flame placed directly beneath it. The whole arrangement is supported by a tripod.

(5) Copper oxide tube; a brass tube 12 inches long and ⅜ of an inch in diameter, containing granular copper oxide in that part of the tube which is subjected to redness. This tube is water-jacketed, as recommended by Dr. Sargent.[1] If these water-coolers are made over copper tubes, large enough in diameter to allow the copper oxide tube to slide freely through them, but not too loosely, it will be found a simple matter to replace the copper oxide tube at any time. These coolers are best supplied with water directly from the tap, the outlet of one cooler being connected to the inlet of the other by glass tubing and rubber connections, and the waste water carried to a suitable drain pipe, near at hand. The copper oxide tube rests upon a tripod and over it is

[1] This Journal, **22**, 277.

placed a piece of fire-brick, cut so as to form an arch over the tube, and retain the heat. The copper oxide tube is heated for a length of 3 inches to a good red heat, and if the Bunsen flame will not do this, a blast is used allowing it to strike the fire-brick first and curl around the tube.

(6) The next part of the train, is that recommended by Job and Davies,[1] and consists of a U-tube, 6 inch form, containing in the arm nearest the copper oxide tube, thoroughly dehydrated cupric sulphate, and in the other, thoroughly dehydrated cuprous chloride.

(7) A silver sulphate tube containing 10 cc. of silver sulphate solution.

(8) A calcium chloride tube, filled with freshly and thoroughly dehydrated granular calcium chloride.

(9) The potash absorption bulb, same style as used by Dr. Sargent[2] and Job[2] and Davies.

(10) A guard tube of calcium chloride.

The solution of steels is obtained by the use of an acidified solution of double chloride of copper and potassium. The filtration of the carbon is effected as follows. A glass rod, small enough in diameter to pass through the stem of a carbon filtering tube $\frac{7}{8}$ by 3 inches, is flattened out at one end as recommended by Shimer.[3] Upon this flattened end is supported a platinum perforated disk smaller than $\frac{7}{8}$ inch, so that it just about clears the sides of the tube when dropped into place. The glass rod and platinum or porcelain disk are put into place in the carbon filtering tube, a layer of dry asbestos previously washed and ignited is made upon the disk, and a little short-fiber asbestos suspended in water is then poured upon it, until a felt of about $\frac{1}{8}$ inch or more is formed.

The filtering is done upon this bed, using suction. When the washings are completed, the suction is turned on hard and the felt sucked dry. The platinum disk carrying the asbestos felt and carbon residue is then pushed to the top of the funnel tube, and as a general thing it will be found to wipe the sides of the tube free from carbon; when near the top it is pushed forward with a sudden jerk, carrying it out of the tube. It may then be placed upon a watch-glass, put in the oven and dried. The asbestos felt

[1] This Journal, **22**, 791.
[2] *Loc. cit.*
[3] *Loc. cit.*

and carbon should be transferred from the tube to the watch-glass just as soon as the felt has been freed from excess of water, otherwise the carbon may dry upon the sides of the filtering tube and cannot be wiped clean when the asbestos plug is pushed forward, and this will necessitate the use of a little ignited asbestos to wipe the sides of the tube, the only objection to any form of filtration for carbon which necessitates a transference of the carbon residue.

With such an arrangement 6 or 8 carbons might be filtered at one time, or in the time it generally takes to filter one, by simply having 6 or 8 tubes suitably connected to a source of suction. With a little practice it will be found that it is not often necessary to clean out the tube with an extra piece of asbestos.

After the carbon plug is dry, it is transferred, carbon side down, to the platinum crucible and it is best, as recommended by Shimer,[1] to have a thin platinum disk in the bottom of the crucible. The platinum disk used for filtering is removed from the asbestos felt before it is introduced into the crucible, a very easy operation as the felt in drying turns up at the edges so that it may be picked up with forceps and transferred to the crucible. The felt carrying the carbon is pressed against the bottom and sides of the crucible, and if it was found necessary to wipe the sides of the filtering tube with ignited asbestos this too is added, keeping it close to the sides of the crucible. If now a platinum disk, the same as used in filtering, is dropped upon the felt it will greatly aid in keeping the heat in the bottom of the crucible, although it is by no means necessary.

The asbestos washer is now moistened with a little water (about 5 or 6 drops), as is also the contact flange of the cup, using the wet finger; the cup is now screwed into place and drawn up tight. The apparatus is placed on the asbestos board, over the tripod, the water connections made, and the air-inlet and air-outlet tubes connected to the absorption train. The copper oxide tube having in the meantime been heating, air is now turned on and allowed to flow at the rate of 4 bubbles per second for five minutes, when the weighed potash bulb is introduced in the train and the Bunsen flame is brought under the combustion crucible; ¾ to 1 inch may easily be brought to a good red heat. The author has been using

[1] *Loc. cit.*

fifteen minutes for a combustion and fifteen for aspiration, with an air flow of 4 bubbles per second during combustion and 5 during aspiration, and combustions may be made in less time than this, as the combustion is completed in from ten to fifteen minutes, and it is simply a matter of washing all the carbon dioxide from the train in as short a time as possible and using the least amount of air.

Blank determinations as obtained with this apparatus do not run over 0.0005 gram, and have been as low as 0.0002 gram. The results obtained on standard samples, the carbon of which was determined by combustion in platinum and porcelain tubes, checked very closely and a series of determinations on the same sample were very concordant.

The following changes might be made in the apparatus: (1) It could be made of aluminum. (2) The upper outside face of both cup and casing might be knurled, affording a better hold in putting together. (3) The cup might be closed and provided with water inlet and the outlet tube connected to the water-jacket of the copper oxide tube, thereby reducing the number of water connections. (4) The air inlet tube should be bent a little towards the center and away from the walls of the crucible. The original cost of the above form of apparatus need not exceed $5, not of course including the crucible, and can be made in any machine shop.

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OCCURRENCE OF SALICYLIC ACID IN FRUITS.[1]

BY F. W. TRAPHAGEN AND EDMUND BURKE.

Received November 13, 1902.

FOR the past twelve months or more, tests for salicylic acid in various fresh fruits have been carried on in the laboratory of the Montana Experiment Station with the result of showing its almost constant presence in extremely small quantity.

So far as we know the only similar work has been done by Portes and Desmouliere[2] who report its presence to the extent of

[1] Read at the November meeting of the New York Section of the American Chemical Society.

[2] *J. Pharm. Chim.*, **14**, 342.

a milligram to the kilogram of strawberries. Desmouliere, in his doctorate thesis in the Université de Paris, also reports its presence in raspberries, mulberries and licorice root.[1] This, so far as we know, covers all the work done on fresh fruit outside of this laboratory. It is probable that the acid is present as the methyl salt, which is well known in oil of wintergreen, though we have not yet taken steps to prove this.

Among the fruits from which we have obtained the salicylic acid reaction are the following: strawberries, raspberries (both red and black), blackberries, currants, plums, black cherries, apricots, peaches, Concord grapes, crab-apples, standard apples and oranges. In a few instances we have made this work quantitative with the following results:

Currants, 0.57 mg. acid per kilo of fruit.

Cherries, 0.40 mg. acid per kilo of fruit.

Plums, 0.28 mg. acid per kilo of fruit.

Crab-apples, 0.24 mg. acid per kilo of fruit.

Grapes, 0.32 mg. acid per kilo of fruit.

These values, however, are not absolute but only comparative, and represent the amount which we have succeeded in extracting in each case. We distilled the fruit with phosphoric acid, extracted the distillate with ether, took up with a small amount of water, and applied the ferric chloride test after the ether had evaporated. Check analyses made with known amounts of salicylic acid showed that not nearly all of the acid was extracted by this method. We have also found the salicylic acid reaction to be given by tomatoes, cauliflower and string beans.

It seems to us that the bearing of this work is very important, particularly as regards the investigations of food chemists. While these very small quantities may not react to the tests for salicylic acid as usually applied, especially in view of the small amount of material generally worked upon (25 grams), yet a knowledge of its wide distribution may save reporting, on occasions, materials as adulterated to which salicylic acid has not been added. Knowing that salicylic acid may occur in many of the substances, either a quantitative determination will be necessary in each case or it will be well to report only on strong reactions. We were led to this investigation by the protest of a well-known

[1] *J. Pharm. Chim.*, **16**, 86.

reputable firm in whose currant jelly we reported salicylic acid but which was present in no greater quantity than we have since found it in the fresh currants. A similar experience was lately had in one of the state laboratories for food control.

In addition to the above work we are studying the distribution of benzoic acid in fruits and vegetables, and hope to be able to publish our results within the year.

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BOZEMAN, MONT.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY—U. S. DEPARTMENT OF AGRICULTURE, NO. 46.—SENT BY H. W. WILEY.]

IODINE ABSORPTION OF OILS AND FATS.

A COMPARISON OF METHODS.

BY L. M. TOLMAN AND L. S. MUNSON.

Received December 22, 1902.

THE Hübl method has been used almost entirely for this determination but it has several faults. First, the solution rapidly loses in strength so that it will change materially during a determination, and after standing a week or so becomes too weak for use. Second, it is so slow in its reaction with some of the oils, such as linseed, that a very serious error is brought about by the change in the strength of the solution during the time of reacting.

Wijs[1] showed how considerable this error might be, and the following table taken from his work shows how much difference the time of titrating the blank makes in the iodine number.

TABLE I.—IODINE NUMBERS OF LINSEED OIL BY HÜBL METHOD.

Time of absorption. Hours.	Blank titrated at beginning.	Blank titrated at end.
2	173.74	.....
7	177.65	170.39
24	181.89	163.16

These figures show a decrease in the iodine number after seven hours, if the blank is titrated at the end of the determination. Wijs considers that the true iodine number in this case lies between 173.7 and 181.89. This variation is a very serious objection

[1] *Chem. Rev. Fett. u. Harz. Ind.*, **6**, 6 (1899).

to the Hübl method, and, on such oils as have a high number, greatly reduces the value of the determination and probably accounts for the wide range of figures obtained by different analysts.

A solution that would remain permanent would completely remove this source of error. Two new solutions have been proposed as substitutes for the Hübl, and it is claimed for both that they change but little with age, and are also more rapid in their action than the Hübl solution, yet give results agreeing very closely with those obtained by the Hübl method.

The Wijs[1] solution is iodine chloride dissolved in glacial acetic acid. The Hanus[2] solution is iodine bromide dissolved in glacial acetic acid. Wijs[3] claims that a solution, made up with acetic acid (99 per cent.) showing no reduction with bichromate and sulphuric acid and containing a very slight excess of iodine in order to prevent the presence of any iodine trichloride, remained practically constant for eighteen months. Twenty-five cc. which were neutralized by 47.3 cc. N/10 thiosulphate at the beginning, at the end required 46.9 cc. N/10 thiosulphate. Lewkowitsch[4] found that after five months the strength of such a solution was practically unchanged. Our experience has been the same. A solution remained practically without change for a month.

Hanus[5] showed that a solution of iodine bromide in glacial acetic acid changes only very slightly in three months, and our experience has corroborated this claim. The Hanus solution was prepared as suggested by Hunt;[6] 13.2 grams iodine were dissolved in 1000 cc. glacial acetic acid (99.5 per cent.), which gave no reduction with bichromate and sulphuric acid, and then enough bromine was added to double the halogen content of the solution. This takes approximately 3 cc. of bromine. The iodine solution should be cold when the bromine is added. Forty cc. of a solution prepared as directed above contained 1.0300 grams of iodine: a month later it contained 1.02791 grams. This difference might easily be due to the difference in temperature at the time the 40 cc. were measured. In order to get strictly accurate results a

[1] *Ber. d. chem. Ges.*, **31**, 750 (1898).
[2] *Ztschr. Nahr. u. Genus.*, **4**, 913 (1901).
[3] *Ibid.*, **5**, 499 (1902).
[4] *Analyst*, **24**, 257 (1899).
[5] *Ztschr. Nahr. u. Genus.*, **4**, 916 (1901).
[6] *J. Soc. Chem. Ind.*, **21**, 454 (1902).

number of 20 cc. portions were measured into stoppered flasks and titrated from day to day. The following table shows that the solution is constant:

TABLE II.

Time of standing. Days.	N/10 thiosulphate = 20 cc. iodine. Cc.
1	45.50
2	45.50
3	45.55
5	45.50
6	45.55
8	45.60

This is enough to show that either of the solutions is satisfactory and very much better than the Hübl in retaining its strength.

The second objection to the Hübl solution is slowness of reaction. The time recommended to be allowed in order to complete the reaction is variously given by different authors from two to twenty-four hours. Allen[1] recommends two hours. The official method of the Association of Official Agricultural Chemists requires three hours. Lewkowitsch[2] recommends four hours. Wijs[3] showed that with linseed oil the absorption was not complete in seven hours and perhaps longer. These different methods will give varying results. Wijs recommends, when his solution is used, fifteen minutes for non-drying fats and oils, thirty minutes for semidrying oils, and one hour for drying oils.

The following table showing results obtained with both Hanus' and Wijs' solutions substantiates these claims.

TABLE III.—TIME NECESSARY FOR COMPLETE ABSORPTION OF IODINE.

Lab. No.	Kind of oil.	Iodine numbers by Hanus' method. 15 min.	30 min.	1 hr.	Iodine numbers by Wijs' method. 15 min.	30 min.	1 hr.
773	Cocoanut	8.7	8.6	....	....	....	....
22,077	Konut.....	6.4	6.4	....	....	....	....
1,170	Butter.....	35.2	35.4	....	....	....	....
1,168	"	35.4	35.5	....	35.8	35.9	36.0
	Oleo oil	43.2	43.4	....	....	....	....
4	Oleomargarine .	52.4	51.8	....	....	....	....
5	" .	51.9	52.1	....	52.9	....	53.0
9	" .	64.6	65.1	....	....	....	....
1	" .	52.2	52.4	....	....	....	....

[1] "Commercial Organic Analysis," Vol. II, Part 1, p. 64.
[2] "Chemical Analysis of Oils, Fats and Waxes," 1898, p. 173.
[3] *Chem. Rev. Fett. u. Hartz. Ind.*, **6**, 7 (1899).

Lab. No.	Kind of oil.	Iodine numbers by Hanus' method. 15 min.	30 min.	1 hr.	Iodine numbers by Wijs' method. 15 min.	30 min.	1 hr.
	Oleomargarine	80.4	80.5	....	....	....	....
23,606	Lard oil	70.0	69.7	....	....	....	....
798	Olive oil	90.1	90.4	90.3	90.0	91.2	90.9
960	" "	82.1	81.7	82.2	82.6	82.6	82.5
833	" "	86.5	86.5	86.5	86.5	86.7	87.2
772	Peanut	96.0	97.4	97.7	98.8	99.0	99.0
777	Mustard	125.0	126.0	126.0	126.5	126.5	128.0
771	"	....	119.4	120.0	....	118.0	118.2
776	"	....	105.0	105.0	....	104.3	104.6
775	Rape	....	107.4	107.5	....	105.8	105.7
770	Corn	....	116.8	117.6	117.1	116.1	118.5
774	Poppy	136.8	137.4	138.4	138.8	138.9	139.1
1,162	Linseed	....	186.3	186.2	183.8	190.2	188.7

For butter, lard, oleomargarine, and olive oil, the reaction is practically complete in fifteen minutes. With cottonseed, sesame, and mustard, thirty minutes are necessary, while with poppy and linseed one hour gives the best results. There seems to be practically no difference between the two solutions in respect to speed of action. Tables IV and V give the results obtained by ourselves on a number of oils by all three methods. Table VI is a compilation of the data available on the three methods.

TABLE IV.—IODINE NUMBERS OF OILS AND FATS.

Lab. No.	Oils.	Hübl's number, 3 hrs.	Wijs's number, 30 min.	Hanus's number, 30 min.	Difference between Wijs and Hübl.	Difference between Hanus and Hübl.
	Non-drying.					
	Cocoanut	8.93	9.05	8.60	+ 0.12	— 0.33
	Konut	6.09	6.43	6.40	+ 0.34	+ 0.31[1]
1,170	Butter	35.3	36.2	35.3	+ 0.90	+ 0.00
1,168	Butter	34.8	35.9	35.4	+ 1.10	+ 0.60
	Oleo oil	42.6	43.5	43.3	+ 0.90	+ 0.70
1	Oleomargarine	53.6	53.5	52.3	— 0.10	— 1.30
4	"	52.8	53.7	52.2	+ 0.90	— 0.60
5	"	52.5	52.9	52.0	+ 0.40	— 0.50[1]
9	"	66.3	66.0	64.8	— 0.30	— 1.50
23,606	Lard oil	69.3	70.5	69.8	+ 1.20	+ 0.50
487	" "	73.7	74.5	73.9	+ 0.70	+ 0.20[1]
1,181	Magnolia oil	81.7	79.4	78.9	— 2.30	— 2.80
1,182	" "	76.1	75.6	74.0	— 0.50	— 2.10
772	Peanut "	96.3	99.0	97.4	+ 3.00	+ 1.10
1,149	" "	94.5	95.2	94.1	+ 0 70	— 0.10
492	" "	107.7	109.5	107.7	+ 1.80	+ 0.00[2]

[1] Commercial oils.

[2] Adulterated with cottonseed.

Lab. No.	Oils.	Hübl's number, 3 hrs.	Wijs's number, 30 min.	Hanus's number, 30 min.	Difference between Wijs and Hübl.	Difference between Hanus and Hübl.
770	Mustard oil ..	110.4	118.5	115.5	+ 8.10	+ 5.10
771	" " ..	113.0	118.2	116.8	+ 5.20	+ 3.80
776	" " ..	98.4	104.3	103.8	+ 5.90	+ 5.40
486	" " ..	103.5	112.5	110.2	+ 9.00	+ 6.70[1]
495	" " ..	106.4	117.3	114.8	+10.90	+ 8.40[1]
775	Rape oil	101.3	105.7	105.2	+ 4.40	+ 3.80
490	" "	100.2	104.1	102.8	+ 3.90	+ 2.60[1]
	Semi-drying and drying.					
	Sunflower	106.4	109.2	107.2	+ 2.80	+ 0.80
1,159	Cottonseed oil .	103.8	105.3	105.2	+ 1.50	+ 1.40
1,160	" " .	106.2	107.3	107.8	+ 1.10	+ 1.60
1,161	" " .	104.8	106.2	106.7	+ 1.40	+ 1.90
489	Sesame oil	106.4	107.0	106.5	+ 0.60	+ 0.10[1]
444	Corn "	119.0	123.2	120.2	+ 4.20	+ 1.20[1]
491	" "	119.0	122.2	119.6	+ 3.00	+ 0.40[1]
777	" "	123.3	129.2	126.0	+ 5.80	+ 2.70
493	Poppy "	133.4	135.2	132.9	+ 1.80	— 0.50[1]
774	" "	134.9	139.1	138.4	+ 4.20	+ 3.50
1,162	Linseed "	169.8	186.5	184.5	+16.70	+14.70[1]
1,188	" " ..	179.5[2]	188.7	183.7	+ 9.20	+ 4.20

It will be seen from these results that for oils and fats with an iodine number under 100 there is little difference between the three methods. For practical purposes they are the same. But this is not so true for the oils with higher iodine numbers. With mustard and rape oil there is a marked difference, 8.4 numbers higher with Hanus's and 10.9 numbers higher with Wijs's method. It is with these oils and linseed oil that there is the widest variation, but there can be little doubt that the higher numbers obtained by the Hanus and Wijs methods are the more correct.

TABLE V.—IODINE NUMBERS OF OLIVE OILS.

Lab. No.	Hübl's number, 3 hrs.	Wijs's number, 30 min.	Hanus's number, 30 min.	Difference between Wijs and Hübl.	Difference between Hanus and Hübl.
795	89.7	90.9	90.4	+1.2	+0.7
796	89.7	90.6	90.0	+0.9	+0.3
797	89.8	91.4	90.0	+1.6	+0.2
798	89.7	91.1	90.4	+1.4	+0.7
960	80.9	82.5	81.7	+1.6	+0.8
833	84.8	86.7	86.5	+1.9	+1.7

[1] Commercial oils.

[2] Four hours for Hübl determination.

Lab. No.	Hübl's number, 3 hrs.	Wijs's number, 30 min.	Hanus's number, 30 min.	Difference between Wijs and Hübl.	Difference between Hanus and Hübl.
831	85.2	86.7	85.9	+1.5	+0.7
832	84.9	86.5	85.9	+1.6	+1.0
834	84.5	86.1	85.1	+1.6	+0.6
936	81.8	82.8	82.8	+1.0	+1.0
933	80.6	81.6	81.1	+1.0	+0.5
835	82.7	83.1	82.6	+0.4	−0.1
962	81.2	81.5	80.9	+0.3	−0.3
955	82.6	83.6	83.1	+1.0	+0.5
952	81.3	82.2	81.8	+0.9	+0.5
840	86.3	87.8	86.7	+1.5	+0.4
935	80.5	80.9	81.6	+0.4	+1.1
953	79.2	79.9	80.6	+0.7	+1.4
958	81.8	83.1	81.8	+1.3	0.0
959	81.4	83.4	81.9	+2.0	+0.5
954	86.1	87.7	86.3	+1.6	+0.2
934	81.1	82.4	82.3	+1.3	+1.1
956	84.5	85.9	85.6	+1.4	+1.1
932	80.5	82.0	81.4	+1.5	+0.9
961	80.8	82.3	81.1	+1.5	+0.3
836	86.0	87.7	86.6	+1.7	+0.6
931	80.7	82.2	81.5	+1.5	+0.8
838	86.1	87.9	87.1	+1.8	+1.0
839	89.0	91.3	89.9	+2.3	+0.9
837	84.0	...	84.9	...	+0.9
673	83.3	84.1	82.6	+0.8	−0.7
841	86.9	88.0	87.3	+1.1	+0.4
842	87.2	88.1	87.1	+0.9	+0.1
843	85.1	86.6	85.6	+1.5	+0.5
844	84.2	85.0	84.2	+0.8	0.0
1,091	81.9	83.4	82.0	+1.5	+1.10
		Average, 36 samples,		+1.2	+0.59

The iodine numbers of the thirty-six samples of olive oils of known purity obtained by the three methods are given in this table. The maximum difference between Wijs and Hübl is 2, the Wijs method always giving higher results. On the thirty-six samples the Wijs method gave an average of 1.2 numbers higher.

The Hanus method gave a maximum of 1.4 numbers higher than Hübl, with an average of 0.59 number higher. This gives the Hanus solution a very slight advantage over the Wijs and this difference seems to hold good on all the oils—the Hanus being slightly nearer the Hübl than is the Wijs.

TABLE VI.—IODINE NUMBERS BY DIFFERENT METHODS.

Variety of oil.	Hübl's number.	Wijs's number.	Hanus's number.	Difference between Hübl and Wijs.	Difference between Hübl and Hanus.	Analyst.
Cocoanut..	9.03	....	9.03	....	0.0	Hanus.
Butter	30.7	....	30.6	....	—0.1	"
Lard.....	56.4	....	56.9	....	+0.5	"
Peanut....	88.3	....	88.4	....	+0.1	"
"	87.2	87.2	...	0.0	....	Wijs.
"	91.8	93.4	91.6	+1.6	—0.2	Hunt.[2]
Rape.....	99.3	...	98.8	....	—0.5	Hanus.
"	102.9	103.3	....	+0.4	....	Wijs.[1]
"	103.0	102.1	101.9	—0.9	—1.1	Hunt.[2]
Sunflower.	117.8	119.0	....	+1.2	....	Wijs.[1]
Sesame ...	110.3	111.7	....	+1.7	....	"
" ...	107.1	....	107.5	....	+0.4	Hanus.
Corn.....	124.8	128.4	....	+3.6	....	Wijs.[1]
Poppy	122.4	....	122.6	....	+0.2	Hanus.
"	134.6	....	135 2	....	+0.6	"
"	119.6	119.6	....	0.0	....	Wijs.[1]
Linseed ...	174.8	177.3	174.5	+2.5	—0.3	Hunt.[2]
" ...	180.9	182.1	....	+1.2	....	Wijs.[1]
" ...	170.2	....	171.0	....	+0.8	Hanus.

These figures show practically the same results as the previous tables although not quite so wide a variation, which may be somewhat accounted for by the fact that four hours were used in the Hübl determinations, which gives a little higher figure than the three hours on the higher-absorbing oils. These results show very little choice between the two proposed substitutes for the Hübl method. The Hanus gives results a little closer to the Hübl figures but the difference is of practically no consequence. Its chief advantage over the Wijs is in the ease of preparation. Iodine trichloride is a rather rare reagent and the preparation of the iodine chloride by passing chlorine gas into the acetic acid solution of iodine until the halogen content is doubled is a somewhat tedious operation compared with the addition of bromine. On this account we favor the Hanus solution.

With this change of method, a new set of figures will have to be obtained for the semidrying and drying oils, and such oils as mustard and rape with high iodine absorption. For the butters, lard and olive oil the Hanus method compares satisfactorily with the Hübl. The stability of the solution does not lessen the need

[1] Seven minutes used in determination.
[2] One hour used in determination.

of blanks for each set of determinations. The high coefficient of expansion of glacial acetic acid, 0.00115 for 1° C., makes an appreciable error if a slight change of temperature takes place, as will be seen from the following table.

TABLE VII.

Temperature. °C.	40 cc. iodine monobromide in N/10 thiosulphate.
16.0	92.05
17.5	91.85
18.5	91.80
21.5	91.35
24.5	91.10
27.0	90.80
11°	1.25 cc.
change	decrease.

A change of ± 1° C. gives a change of ∓ 0.11 cc. in the amount of N/10 thiosulphate necessary to neutralize 40 cc. of the iodine solution, so that a blank titration of the iodine solution could easily vary 1 cc. N/10 thiosulphate in a day, which would completely vitiate the results.

DOES CHOLESTEROL OCCUR IN MAIZE OIL?

BY AUGUSTUS H. GILL AND CHARLES G. TUFTS.

Received December 31, 1902.

ACCORDING to Hoppe-Seyler[1] and to Hopkins,[2] cholesterol occurs in maize oil. As there is evidence of the occurrence of this substance in no other vegetable oil, except olive oil, this is interesting, and of possible importance as a means of detecting maize oil in mixtures with other oils. The statement of Hoppe-Seyler was made before this group of bodies was clearly differentiated, however, and the melting-point ascribed by Hopkins to the alcohol found by him in maize oil is not the true melting-point of cholesterol. The difference in the melting-points is shown below. Cholesterol, 146°-147°;[3] "cholesterol" from maize oil, 137°-137.5°.[3] Hopkins used no other means of identification except the color

[1] *Bull. Soc. Chim* [2], **6**, 342 (1866); *Medicin.-chem. Untersuch.*, **1**, 162.

[2] This Journal, **20**, 948 (1898).

[3] Wislicenus and Moldenhauer: *Ann. Chem.* (Liebig), **146**, 179 (m. p. 147°); Reinitzer: *Monatsh. Chem.*, **9**, 422 (m p. 147.5°); Hesse: *Ann. Chem.* (Liebig), **192**, 177 (1878) (m. p. 145°-146°); Salkowski: *Ztschr. anal. Chem.*, **26**, 567 (m. p. 146°); Bömer: *Ztschr. Untersuch. Nahr. u. Genus.* (1898), p. 81 (average m. p. of fifty-two samples, 146.4°-147.3°).

reactions, which are not reliable. These considerations seemed to offer a field for investigation.

The method employed for isolating the compound was substantially that of Forster and Riechelman,[1] which consists in the extraction of the oil with 95 per cent. alcohol and separation of the substance sought from the saponified alcoholic solution. Four hundred grams of oil were extracted with 300 cc. of alcohol in successive portions of 100 cc. each, the oil being boiled half an hour with each portion in a liter flask provided with a reflux condenser. After cooling, each portion of alcohol was drawn off by a separatory funnel and the combined extracts were saponified by boiling two hours with 40 cc. of alcoholic soda 1:3. The greater part of the alcohol was then distilled and the residue, transferred to an evaporating dish, was carried to dryness on a water-bath. The dried and powdered soap was extracted with three portions of ether of 200 cc. each by shaking in a wide-mouthed stoppered bottle; after settling, the ether was decanted through a filter. The filtered extract was distilled and the residue purified by repeated recrystallization from alcohol.

In applying this method to different portions of oil, it was found that while extraction of the dry soap was tedious and attended by loss of ether and, furthermore, gave a product which was quite impure, the extraction of the aqueous solution of the soap was more rapid, more nearly complete and yielded at once a crystalline residue of a fair degree of purity. For a quantity of oil weighing 600 grams, good results were obtained by dissolving the soap in 250 cc. of water and extracting the solution with ether in 100 cc. portions; after four or five extractions the solution was found practically exhausted. It was found advantageous to distil from the alcoholic extract of the oil a considerable portion of the alcohol before saponification and to use alcoholic potash rather than soda. In this way pure characteristic crystals can be obtained without difficulty from 50 grams of oil.

In working with large quantities of oil, from 500 to 1800 grams, the extraction with alcohol was successfully carried out in an ordinary tin (gallon) can heated on a water-bath. A half-inch brass tube was soldered into the cover and connected by a short piece of stiff rubber tubing with a reflux condenser; the rubber

[1] *Ztschr. für öffent. Chem.*, **3**, 10.

tube was used to permit thorough shaking of the can during extraction. The cover was sealed by winding about it before insertion a string smeared with a dextrin paste.

Altogether about 4 kilos of maize oil were examined according to the method outlined above; based on the extraction of one portion of 600 grams, the yield of fully purified crystals was 0.22 per cent. These melted, when dried at 100°, at 138°-138.3°; when dried *in vacuo*, at 137.5°-138°; and after 18 months, at 128°-130°. To the naked eye the crystals from alcohol, appeared to be broad needles; under the microscope they were found made up of thin laminae much longer than broad and pointed at the ends.

From Raoult's method of molecular weight determination, results were obtained increasing with the concentration, showing association in benzene, the solvent used.

The acetate was made by boiling for one hour with an excess of acetic anhydride. The product was washed with water and then with hot alcohol. From the ethereal solution crystals were precipitated by alcohol, which, purified by recrystallization and dried at 100°, melted sharply at 127.1°; they seemed less soluble in alcohol than the corresponding substance obtained from olive oil.

The propionate was made like the acetate and was purified similarly. When dried at 100°, the crystals melted at 108.4°; they were more soluble in alcohol than were those of the acetate.

The benzoate was made by fusion with an excess of benzoic anhydride, the mixture being heated in an open tube to initial boiling. The product was boiled some minutes with alcohol and was then thrown on a filter and washed with boiling alcohol and with small portions of warm ether. The yield was small but there was no attendant discoloration and the crystals seemed pure. On crystallization from ether they formed oblong rectangular plates, often with re-entrant angles. The melting-point was 142°-142.5°.

The color reactions were as follows. In dilute chloroform solution, sulphuric acid produced a rather bluish pink, while the acid layer was yellow. In concentrated solution, the acid layer was yellow and the chloroform a blood-red which became purple on standing. In dilute acetic anhydride solution, sulphuric acid produced a clear green which, on standing, changed to a pure yellow. In concentrated solution the color was a deep bluish

green, permanent for twenty-four hours. Though these reactions and those of the high-melting alcohols of wool grease are too much alike to be of value in analysis, the following differences were observed. On standing, the chloroform layer of Salkowski's test is blood-red with a concentrated solution of wool grease alcohol, and purple with the alcohol from maize oil. With Lieberman's test, in dilute solution, wool grease alcohol gives a bluish green which becomes reddish yellow on standing, while maize oil gives a clear green changing, on standing, to a yellow free from red.

The above results seem sufficient to prove that the alcohol of maize oil is not cholesterol. As shown by the following comparative table, the compound studied is undoubtedly identical with the compound found in wheat and rye and described by Burian under the name "Sitosterol."[1] It is also probably identical with the "Hydrocarotin" of Reinitzer.[2]

MELTING-POINTS OF SITOSTEROL AND ITS ESTERS.

Sitosterol.	From wheat.	From maize oil.	Hydrocarotin.
Sitosterol.....	137.5°	138°	137.4°
" acetate.....	124.5°–127°[3]	127.1°	127.6°
" benzoate...	145.0°–145.5°	142.0°–142.5°	144°
" propionate.	108.5°	108.4°	....

SITOSTEROL, A POSSIBLE TEST FOR MAIZE OIL.

BY AUGUSTUS H. GILL AND CHARLES G. TUFTS.

Received December 31, 1902.

WHILE the presence of cottonseed oil in other oils is easily detected, the recognition of adulteration of cottonseed oil itself is less simple. The addition of many oils would be shown by their effect on the usual analytical constants, but with maize oil these values show so little divergence from those of pure cottonseed oil that detection of admixture is difficult. Since, however, maize oil contains sitosterol[4] while cottonseed oil contains phytosterol, it seemed that a test might be based upon this difference.

In the preceding article it was observed that the acetate of sitosterol from maize oil seemed rather less soluble in alcohol than

[1] *Monatsh. Chem.*, **18**, 551-574 (1897).
[2] *Ibid.*, **7**, 597-608.
[3] Softened at 124.5° and melted at 127°.
[4] See the preceding article.

the acetate prepared from olive oil. It was thought that if a relatively small amount of maize oil were to be mixed with an oil known to contain phytosterol, it would be possible to secure by recrystallization of the acetates a portion whose melting-point would approach that of sitosterol acetate. The following trials were therefore made.

A pure cottonseed oil, a cottonseed oil containing 10 per cent. of maize oil, and one containing 20 per cent. of maize oil were extracted, using 50 gram portions, by boiling twenty minutes at a reflux condenser with 100 cc. of 95 per cent. alcohol. The mixtures were then run into separatories and left over night. The clear alcoholic layer was drawn off, boiled fifteen minutes with 75 cc. of half normal alcoholic potash, evaporated to dryness and the residue dissolved in 40–50 cc. of water. The cooled soap solution was shaken out with 75 cc. of ether and 3 cc. of alcohol, and the extract was washed three times with water and evaporated. The yield by this process, which was not expected to give complete extraction, was as follows: Pure cottonseed oil, 0.095 per cent.; 10 per cent. maize oil, 0.12 per cent.; 20 per cent. maize oil, 0.164 per cent.

The crystals obtained were acetylated without further purification by boiling one hour with an excess of acetic anhydride in a beaker covered with a watch-glass containing a little water. The excess of anhydride was evaporated on the water-bath and the acetates recrystallized from alcohol. In recrystallizing, the acetates were dissolved in hot 95 per cent. alcohol and water was then added drop by drop as long as the solution remained clear after shaking; as soon as there were indications of permanent opalescence a few drops of alcohol were added until the solution was perfectly clear. The beaker was then set aside and the crystals subsequently formed were filtered off, dried at 100° C. and the melting-point determined. Proceeding in this way the melting-points shown on the sixth, and subsequent, crystallization were: Pure cottonseed, 120°-121°; 10 per cent. maize, 121.5°-122.5°; 20 per cent. maize, 124°-125°. By dissolving the acetates in hot 95 per cent. alcohol just sufficient for solution and then chilling, there was obtained from the 20 per cent. oil after four crystallizations a portion which showed the melting-point 126°-127°; the melting-point of the acetate from the 10 per cent. oil was unchanged.

The crystals deposited on slow cooling from 95 per cent. alcohol were, in the case of pure cottonseed, transparent flat needles; the 20 per cent. maize oil gave crystals which beside these needles, showed an opaque, white, and more granular form; the crystals from the 10 per cent. oil resembled those from the pure cottonseed oil.

Portions of the crystals obtained from the dilute alcohol, as described above, were allowed to crystallize from a little 95 per cent. alcohol on glass slides and examined microscopically. All three acetates showed massed crystals in branching coral forms and also long narrow plates resembling the crystals of phytosterol and of sitosterol. There seemed to be less difference in the crystal forms as thus examined than appeared to the naked eye in the manner of growth of the crystals when slowly deposited.

It would seem that the above test will detect the addition of 10 per cent. of an oil containing sitosterol to an oil carrying phytosterol. While maize oil is the only commercial oil in which sitosterol has so far been definitely reported, Bömer and Winter[1] have obtained acetates melting at 128° and above from linseed, rapeseed and sesame oils; it seems probable that sitosterol is present in more oils than has hitherto been supposed and consequently that the test can only be regarded as conclusive evidence of the presence of maize oil when the analytical constants show the absence of other adulterants.

As the melting-point varies with the method employed, it will be advisable for the operator to determine the melting-point of phytosterol acetate according to the method he himself uses. The above values were determined in straight narrow tubes attached to the bulb of an Alverginat thermometer and suspended in a test-tube of sulphuric acid. This was in turn suspended in a 100 cc. flask about two-thirds full of acid. The flask was supported about an inch above an iron plate heated by a small Bunsen flame. The melting-point was approached fairly rapidly and when within 2° or 3°, the rate of heating was reduced to about 0.2° per minute. The value obtained by Bömer and Winter for the phytosterol acetate from cottonseed oil is 123°-124°, but it may be stated that the values obtained by Bömer for the melting-point of phytosterol are rather higher than those usually reported.

[1] *Ztschr. Unter. Nahr. u. Genus.*, (1898), p. 81.

ON THE RELATION OF THE SPECIFIC GRAVITY OF URINE TO THE SOLIDS PRESENT.

By J. H. Long.

Received December 29, 1902.

Attempts have been made several times to establish a relation between the specific gravity of normal urine and the weight of solids dissolved in the secretion. Such efforts are naturally based on the assumption that while the solids must vary, the variations remain within rather narrow limits and the two most important constituents must change in the same direction. These two important substances are urea and sodium chloride, and the specific gravity observed depends largely on the weight of these bodies present.

From early experiments of Trapp, Haeser and others, repeated later by Neubauer,[1] the relation appeared in general to be definite enough to warrant the use of the so-called coefficient of Haeser in making an approximate estimation of the urine solids from an exact determination of the specific gravity. The direct estimation of solids by evaporation is apparently easy, but unfortunately is liable to an error due to the partial decomposition of urea into ammonium cyanate and that into ammonia and carbonic acid. In addition to this, there is a loss on account of the slightly stable ammonium salts present, which fact is generally overlooked, although its importance is as great as that of the loss from the urea, in some cases. Unless a correction is made for these losses, the error in the final result is rather large, in fact usually larger than is the difference between the true result and that obtained by applying the coefficient of Haeser.

As this is a point of no little importance, I have recently undertaken a new determination of the urinary solids along with the corresponding specific gravities, both determinations being made as accurately as possible. The solid residue was found by the method originally suggested by Neubauer. About 5 grams of urine are evaporated in a porcelain boat which is placed in a horizontal glass tube passing through a steam-bath. The glass tube is connected with a small flask containing standard sulphuric acid in such a manner that a current of dried air may be aspirated through the whole apparatus and carry evolved products into the

[1] *Ztschr. anal. Chem.*, **1**, 166.

standard acid. A subsequent titration with standard alkali and methyl orange shows how much acid has been neutralized by ammonia from the evaporated urine. Three to four hours are given to each evaporation, after which the residue in the boat is allowed to stand about two hours over sulphuric acid before weighing. Neubauer suggested to calculate the ammonia absorbed by the dilute standard acid to urea and add this to the weight of the residue. This has been done in the urine evaporations given below, although the method is not strictly correct, as will be pointed out.

The specific gravities were found by means of a small pycnometer and at a temperature maintained at 25°, with a variation within 0.1°. For possible practical applications, 25° is a much more suitable temperature than is 15° or even 20°. The results are referred to water at 4° as unity and are all given below.

Some preliminary experiments were made to determine the loss in evaporating solutions containing pure urea and certain salts in proportions corresponding to those obtaining for urine. In the first of these I took, with water enough to make about 4 cc.:

	(*a*).	(*b*).
NaCl	0.0930	0.0708
K_2SO_4	0.0077	0.0059
CON_2H_4	0.1467	0.1117
	0.2474	0.1884
Residue recovered	0.2430	0.1851
Urea from ammonia	0.0052	0.0037
	0.2482	0.1888

In the first case, the loss of 5.2 mg. of urea calculated from the ammonia is 3.5 per cent. of the urea present or 2.1 per cent. of the solids. In the second case, 3.7 mg. amounts to 3.3 per cent. of the whole urea, or 2 per cent. of the total solids. Very similar results were found in other tests and need not be given in detail. In the following experiments the effect of a phosphate was determined. With water enough to make about 3.5 cc. in each case, I took:

	(*c*).	(*d*).
NaCl	0.1126	0.0881
K_2SO_4	0.0080	0.0101
HNa_2PO_4	0.0120	0.0120
CON_2H_4	0.1526	0.1927
	0.2852	0.3029

The evaporation was continued three and a half hours, and the ammonia was caught as before.

Recovered directly	0.2830	0.2991
Loss	0.0022	0.0038

The ammonia evolved was found in (*c*) to be equal to 0.5 cc. of N/4 acid and in (*d*) to 0.6 cc. of N/4 acid. Calculating this as urea would more than account for the loss. In this case, however, a part of the carbonic acid from the urea decomposition is held by the alkali phosphate. In (*c*) the total loss was 14.4 mg. per gram of urea, or 1.44 per cent. of the total urea. In (*d*) the loss was 19.2 mg. per gram of urea or 1.92 per cent. of the urea present. These losses are about one-half as great as they were in the absence of the alkali phosphate.

Since the urine is commonly slightly acid and probably from the presence of the dihydrogen phosphate, two further evaporations were made with known amounts of this salt present. It was produced by addition of N/10 sulphuric acid to a solution of the disodium salt. The weights taken, with water enough to make up 4.5 cc., were:

	(*e*).	(*f*).
NaCl	0.1046	0.1053
K_2SO_4	0.0099	0.0100
Na_2SO_4	0.0060	0.0060
H_2NaPO_4	0.0100	0.0100
CON_2H_4	0.1893	0.1900
	0.3198	0.3213
Recovered directly	0.3171	0.3174
Loss	0.0028	0.0039
The ammonia evolved calculated as urea gives	0.0023	0.0037

In such cases, therefore, it seems perfectly proper to add urea to correct the evaporation loss, and the presence of the salts does not appear to increase this appreciably. The decomposition with alkaline phosphate present is probably the same, but the ammonia only is fully liberated.

Below are given the results of fifty-two determinations on the urine of six persons. The samples taken for the tests did not represent the excretion of the whole day but were chosen to represent extreme cases, as far as possible, as the main object of the

investigation was to determine the limits of variations. From other investigations, the average amounts of urea and ammonia excreted by the same individuals, under the same general conditions, had been determined. The urea amounted to 28 grams per liter and the ammonia to 650 mg. per liter. All the tests were made on perfectly fresh urine, from individuals in normal health, consuming an average meat, vegetable and bread diet.

No.	Sp. gr. $\frac{25^{\circ}}{4}$.	Solids in grams per liter.	Loss as urea, grams per liter.	Multiplication factor.
1	1.0199	51.57	2.36	0.259
2	1.0207	51.19	2.95	0.247
3	1.0206	52.33	2.37	0.254
4	1.0189	44.28	2.28	0.234
5	1.0209	53.70	2.14	0.257
6	1.0215	53.10	1.72	0.247
7	1.0227	61.93	2.89	0.272
8	1.0217	53.51	2.46	0.247
9	1.0224	56.54	2.13	0.252
10	1.0180	53.84	2.51	0.299
11	1.0252	66.05	2.56	0.262
12	1.0251	63.54	2.10	0.253
13	1.0226	57.19	1.71	0.253
14	1.0231	60.00	1.95	0.260
15	1.0236	57.38	1.76	0.243
16	1.0236	62.82	2.35	0.266
17	1.0248	59.90	2.74	0.242
18	1.0279	70.73	1.75	0.254
19	1.0230	59.31	1.70	0.258
20	1.0279	75.21	1.96	0.270
21	1.0223	57.48	2.09	0.258
22	1.0177	43.13	1.60	0.244
23	1.0231	63.06	1.92	0.273
24	1.0228	58.37	2.15	0.256
25	1.0284	75.55	1.67	0.266
26	1.0256	73.26	2.34	0.288
27	1.0246	59.75	1.93	0.243
28	1.0191	44.98	2.00	0.235
29	1.0317	79.29	2.31	0.250
30	1.0118	30.02	0.97	0.254
31	1.0237	63.45	4.53	0.268
32	1.0207	51.06	1.73	0.247
33	1.0291	70.90	4.19	0.244
34	1.0243	62.41	2.81	0.257
35	1.0140	37.81	2.01	0.270
36	1.0217	56.56	2.40	0.261
37	1.0225	59.29	2.75	0.264

No.	Sp. gr. $\frac{25°}{4}$	Solids in grams per liter.	Loss as urea, grams per liter.	Multiplication factor.
38	1.0165	45.13	2.49	0.274
39	1.0212	60.01	3.64	0.283
40	1.0155	43.08	2.91	0.278
41	1.0247	62.74	1.62	0.254
42	1.0113	33.47	2.26	0.296
43	1.0161	44.72	2.03	0.277
44	1.0201	53.46	1.61	0.266
45	1.0231	60.95	2.38	0.264
46	1.0225	55.47	0.98	0.242
47	1.0221	56.19	1.83	0.254
48	1.0120	31.69	1.56	0.264
49	1.0160	41.84	1.60	0.261
50	1.0215	53.98	1.70	0.251
51	1.0267	68.91	1.17	0.258
52	1.0160	41.26	2.12	0.258
Mean,	1.0215	55.83	2.19	0.260

The evaporation losses calculated as urea, from the ammonia evolved, are seen to be far greater with the urine than with the artificial mixtures. With an average of 28 grams of urea in the urine the mean loss is evidently about 8 per cent. of this content. While as a matter of convenience it is satisfactory to calculate the loss as urea, a little consideration will show that a part of it must come from other sources. In the evaporation, part of the ammonia present, and possibly sometimes all of it, is driven off and this may be considered as combined as some organic salt and possibly partly as carbonate. In one case the loss would be less and in the other greater than that found by calculation as urea. The usual method of calculation probably represents the average loss, and this has been included in the figures representing the total solids in column 3.

The correspondence between high specific gravity and high solids is a fairly good one in most cases, as shown by the factor in the last column, representing the so-called Haeser coefficient for the temperature of 25°. This factor is obtained by dividing the last three figures of the specific gravity into the weight of solids found. In most cases the variations are not great from the mean value of 0.260, but in Nos. 4, 10, 26, 28, and 42 the divergence is much greater than given by Neubauer. For the *mixed* day's urine the results would be much closer and in any such case the factor 0.260 would not be far from the truth. This factor can be

applied only when the specific gravity is taken at 25°, for which temperature many urinometers are now adjusted. For an instrument graduated to give the specific gravity at 20° referred to water at 4° the factor to be used is 0.234. This was found by making a number of determinations of the specific gravity at the two temperatures and calculating the average coefficient of expansion. Neubauer's average factor is 0.233, based on urine at 15° referred to water at 0°. For the same temperature limits the results are practically identical, which indicates that for normal mixed urine the coefficient has a sharp definite value, and that it may be used as a control in certain kinds of analyses. Results of still greater value in practice may doubtless be secured through the exact determination of a factor for the solids, exclusive of the sodium chloride, that is, for the products of metabolic origin. A series of determinations in this direction is now in progress.

In any case the *exact* determination of the total solids by evaporation does not appear to be possible because of the uncertainty as to how the ammonia loss should be calculated.

My thanks are due to Mr. C. W. Brown, who made many of the determinations given above.

NORTHWESTERN UNIVERSITY,
CHICAGO, December, 1902.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

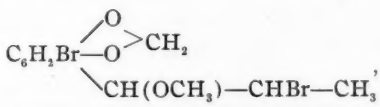
DERIVATIVES OF ISOSAFROL AND ISOAPIOL.

BY F. J. POND AND C. R. SIEGFRIED.

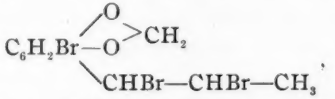
Received January 2, 1903.

IN a previous paper,[1] certain compounds were described which were found to result by the action of hot methyl and ethyl alcohols upon the bromine derivatives of anethol, isosafrol, ethyl isoeugenol and isoapiol; it was stated that these compounds are formed by the replacement of the bromine atom in the side-chain, which stands in the α-position to the benzene ring, by the methoxyl- and ethoxyl-groups. Thus, for example, a compound having the formula,

[1] Pond, Erb and Ford : This Journal, **24**, 327.



results on boiling monobromisosafrol dibromide,



with methyl alcohol. This compound separates from methyl alcohol in large, prismatic crystals, melting at 75° to 76.5°, and it was designated as the methyl alcohol addition-product of dibromisosafrol; it may perhaps be better termed α-methoxy-β-brom-dihydro-bromisosafrol. The analogous ethyl alcohol product was also described. It was likewise shown that corresponding methyl and ethyl alcohol products are formed in a similar manner from anethol dibromide, monobromanethol dibromide, isosafrol dibromide and ethyl isoeugenol dibromide. The alcohol products resulting from anethol and monobromanethol dibromides, isosafrol and ethyl isoeugenol dibromides, having the general formula,

$$R—CH(OR')—CHBr—CH_3,$$

were found to be readily converted by sodium methylate or alcoholic potash into ketones,

$$R—CO—CH_2—CH_3,$$

while the compounds obtained from monobromisosafrol dibromide are remarkably stable towards alkaline reagents, and they do not yield ketones on treatment with sodium alcoholate. The formation of the ketones from the first class of compounds is due to the elimination of the bromine atom in the β-position as hydrogen bromide, and the resulting unsaturated ether is then converted into a saturated ketone by hydrolysis and subsequent molecular rearrangement. In the second class of compounds, the β-bromine atom is not removed by the ordinary alkaline reagents.

Some months after the completion of the work described in the previous paper, Auwers and Müller[1] published an article on certain derivatives of the bromides of eugenol and isoeugenol. These

[1] Auwers and Müller: *Ber. d. chem. Ges.*, **35**, 114.

chemists found that the bromine derivatives of eugenol, which may be represented by the general formula,

$$R—CH_2—CHBr—CH_2Br,$$

are not changed by the treatment with alcohols, aqueous acetone, sodium acetate, organic bases, etc., and that they show no abnormal reactions, but possess the character of ordinary phenols. On the other hand, however, the bromides of isoeugenol, having the formula,

$$R—CHBr—CHBr—CH_3,$$

are at once changed by cold methyl or ethyl alcohol, aqueous acetone and sodium acetate, one atom of bromine being eliminated and replaced by the corresponding radical. In every case the bromine atom which is removed is the one standing in the α-position to the benzene radical; the second or β-bromine atom does not enter into the reaction even at high temperatures or when the reagents, such as sodium acetate, are employed in a large excess. The formation of these compounds is represented by the formulas,

$$R—\underset{\alpha}{CHBr}—\underset{\beta}{CHBr}—CH_3 \rightarrow R—\underset{\alpha}{CH(R')}—\underset{\beta}{CHBr}—CH_3.$$

According to Auwers, therefore, the bromides of isoeugenol possess the character of pseudo-phenols, and in general the bromides of para-alkyl phenols, which contain bromine atoms in the α- and β-positions, react as pseudo-phenols.

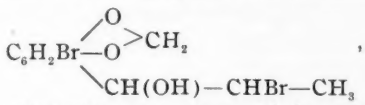
A further point of considerable interest in Auwers's work is that when the ethers or alcohols, resulting by the treatment of isoeugenol dibromide or tribromide, are heated with alcoholic sodium methylate, the β-bromine atom is not eliminated as hydrogen bromide, as was found to be the case with the compounds derived from the bromides of isoeugenol ethers investigated in this laboratory, but it is replaced by the methoxyl-group; this reaction gives rise to ethers of glycols as is represented by the equation,

$$R—\underset{\alpha}{CH(OCH_3)}—\underset{\beta}{CHBr}—CH_3 + NaOCH_3 = NaBr + R—CH(OCH_3)—CH(OCH_3)—CH_3.$$

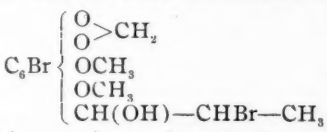
It will be readily seen from the foregoing that Auwers's work is more or less intimately related with the line of investigation which has been conducted in this laboratory for the past three years, the chief difference being that Auwers's researches were carried on with isoeugenol, a compound containing the free phenolic group,

while our work is confined to the ethers of isoeugenol and of other propenyl phenols as anethol, isosafrol and isoapiol. This difference in the constitution of the compounds appears to exert a considerable influence upon the reactions of the substances derived from them, since in no case have we observed the formation of ethers of glycols as described by Auwers.

The experimental work described in this paper is a continuation of our investigations on the action of alcohols and aqueous acetone upon the bromides of isosafrol and isoapiol. From monobromisosafrol dibromide we have prepared a new alcohol,



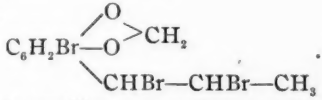
its methyl and ethyl ethers, together with its acetyl and benzoyl derivatives; the same series of compounds is also obtained from monobromisoapiol dibromide, the new alcohol having the formula,



From this alcohol a new ketone has also been obtained.

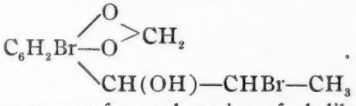
EXPERIMENTAL.

Monobromisosafrol Dibromide,[1]



This compound is readily prepared as previously described by treating an ethereal solution of isosafrol with two molecular proportions of bromine. It separates from a mixture of acetone and ether in colorless crystals, melting at 110° to 111°.

α-Oxy-β-brom-dihydro-bromisosafrol,



A solution of 10 grams of monobromisosafrol dibromide in 50 cc.

[1] Pond, Erb and Ford: This Journal, **24**, 340.

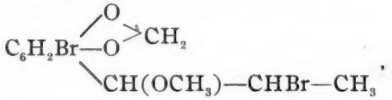
of acetone was heated to boiling and then treated with 15 cc. of water; the aqueous acetone solution was boiled in a reflux apparatus on the water-bath for two hours. The solution at first assumed a red color, which gradually became colorless. On completion of the reaction, the product was poured into an evaporating dish, and, after the evaporation of the acetone, a compound separated as a yellow-colored oil; after standing for about twelve hours, this oil solidified to a white, waxy substance, which was filtered, washed well with water and pressed on a porous plate. The crude compound is exceedingly soluble in alcohol and ether, hence it is best to crystallize first from acetone and to recrystallize from alcohol; it separates from these solvents in beautiful, large crystals, which melt at 89°.

Analysis gave the following results: Calculated for $C_{10}H_{10}O_3Br_2$, C, 35.50; H, 2.95; Br, 47.33. Found, C, 35.75, 35.78; H, 3.21, 3.07; Br, 47.23.

When this compound is boiled with alcoholic potash or sodium methylate, bromine is eliminated; on acidifying the reaction-product with hydrochloric acid and then adding water, an oil is formed. It was expected that this oil would exhibit the ordinary reactions of a ketone, but it failed to yield an oxime or semicarbazone, and its examination must be continued.

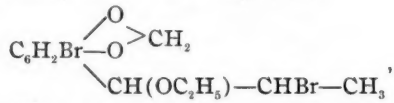
The methyl and ethyl ethers of the foregoing alcohol were described in a previous paper, but they will be briefly reviewed here for sake of completeness.

α-Methoxy-β-brom-dihydro-bromisosafrol,



is formed when a solution of monobromisosafrol dibromide in methyl alcohol is boiled for a short time. It crystallizes from methyl alcohol in large prisms, melting at 75° to 76.5°.

α-Ethoxy-β-brom-dihydro-bromisosafrol,

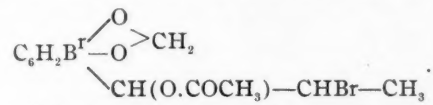


obtained by boiling a solution of isosafrol tribromide in ethyl alco-

hol, crystallizes from alcohol in large crystals, and melts at 58° to 60°.

Boiling, concentrated sodium alcoholate is without action upon these two ethers.

Acetate of α-Oxy-β-brom-dihydro-bromisosafrol,

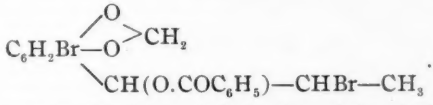


This compound is formed when a solution of 3 grams of potassium acetate in 5 cc. of glacial acetic acid is added to a solution of 10 grams of monobromisosafrol dibromide in 15 cc. of glacial acetic acid, and the whole is boiled for about five minutes.

The cold reaction-product is then poured into water; the compound separates as an oil, which solidifies after standing for about twelve hours. It is crystallized from alcohol, dried on a porous plate, and recrystallized from ethyl acetate; it separates from the latter solvent in fine, white needles, which melt at 73° to 74°.

Analysis gave the following results: Calculated for $C_{12}H_{12}O_4Br_2$, C, 37.89; H, 3.16. Found, C, 37.97, 37.63; H, 3.22, 3.26.

Benzoate of α-Oxy-β-brom-dihydro-bromisosafrol,



In order to prepare this benzoyl derivative of the alcohol, Einhorn and Hollandt's process was employed, since the ordinary Schotten-Baumann method employs alkali, which would lead to a decomposition of the alcohol.

Five grams of α-oxy-β-brom-dihydro-bromisosafrol were dissolved in 15 grams of pyridine, and 3 grams of benzoyl chloride were added slowly, with constant shaking; the mixture was allowed to stand during twenty-four hours, and then poured into dilute sulphuric acid (1:5). The benzoyl derivative separated at first as an oil, but solidified after repeated washing with dilute acid and water, and was crystallized from a mixture of ether and acetone; it forms long, white crystals, melting at 142° to 143°. It is readily soluble in the usual solvents.

Analysis gave the following results: Calculated for $C_{17}H_{14}O_4Br_2$, C, 46.15; H, 3.16. Found, C, 46.27, 46.10; H, 3.24, 3.21.

Monobromisoapiol Dibromide,

$$C_6Br\begin{cases} O \\ O \end{cases}>CH_2$$
$$\qquad\quad \begin{cases} OCH_3 \\ OCH_3 \\ CHBr—CHBr—CH_3 \end{cases}$$

prepared as previously described[1] by the action of two molecular proportions of bromine upon an ethereal solution of isoapiol, crystallizes from acetone and melts at 120°.

α-Oxy-β-brom-dihydro-bromisoapiol,

$$C_6Br\begin{cases} O \\ O \end{cases}>CH_2$$
$$\qquad\quad \begin{cases} OCH_3 \\ OCH_3 \\ CH(OH)—CHBr—CH_3 \end{cases}$$

Twenty grams of monobromisoapiol dibromide were dissolved in 100 cc. of acetone and treated with 30 cc. of water; after boiling for two hours in a reflux apparatus, the acetone was allowed to evaporate and the oily residue was washed well with water. The oil gradually solidified, was washed, dried, and crystallized from alcohol; it separated in large, well-defined crystals, melting at 85° to 86°.

The compound is readily soluble in the usual solvents. When boiled with alcoholic potash, one atom of bromine is removed and a new compound is formed, which will be subsequently described.

Analysis gave the figures: Calculated for $C_{12}H_{14}O_5Br_2$, C, 36.18; H, 3.52; Br, 40.20. Found, C, 36.21, 35.98; H, 3.61, 3.31; Br, 40.34.

The methyl and ethyl ethers of the above-mentioned alcohol are easily obtained by boiling a solution of isoapiol tribromide in methyl or ethyl alcohol.

α-Methoxy-β-brom-dihydro-bromisoapiol,

$$C_6Br\begin{cases} O \\ O \end{cases}>CH_2$$
$$\qquad\quad \begin{cases} OCH_3 \\ OCH_3 \\ CH(OCH_3)—CHBr—CH_3 \end{cases}$$

A solution of 20 grams of monobromisoapiol dibromide in 50 cc.

[1] See Pond, Erb and Ford: This Journal, **24**, 343.

of methyl alcohol is boiled for a few minutes and then poured into a crystallizing dish; the compound separates in large crystals, which melt at 92° to 93°.

Analysis gave: Calculated for $C_{13}H_{16}O_5Br_2$, C, 37.86; H, 3.88; Br, 38.83. Found, C, 38.02, 38.01; H, 3.90, 3.99; Br, 38.78, 38.85.

α-Ethoxy-β-brom-dihydro-bromisoapiol,

$$C_6Br\begin{cases} O \\ O \end{cases}>CH_2$$
$$C_6Br\begin{cases} OCH_3 \\ OCH_3 \end{cases}$$
$$C_6Br\{CH(OC_2H_5)—CHBr—CH_3$$

Twenty-eight grams of monobromisoapiol dibromide were dissolved in ethyl alcohol, and the solution was boiled for ten minutes; on cooling, this compound separated in large crystals, melting at 72° to 73°.

In our previous communication, this compound was described as an oil, and at that time it was impossible to induce the substance to solidify; now, however, we find no difficulty in obtaining a crystalline product at once. We are unable to find a satisfactory explanation for this difference in the behavior of the substance, unless we attribute it to a slightly purer isoapiol tribromide.

The compound was analyzed with the following results: Calculated for $C_{14}H_{18}O_5Br_2$, C, 39.43; H, 4.22. Found, C, 39.59, 39.20; H, 4.00, 4.05.

Hot, concentrated solutions of alcoholic potash and sodium methylate are without action upon these ethers.

Acetate of α-Oxy-β-brom-dihydro-bromisoapiol,

$$C_6Br\begin{cases} O \\ O \end{cases}>CH_2$$
$$C_6Br\begin{cases} OCH_3 \\ OCH_3 \end{cases}$$
$$C_6Br\{CH(O.COCH_3)—CHBr—CH_3$$

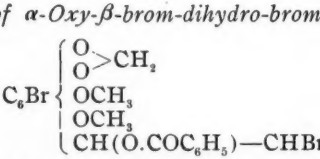
A hot solution of 2.5 grams of potassium acetate in 5 cc. of glacial acetic acid was added slowly, and with shaking, to a warm solution of 10 grams of monobromisoapiol dibromide in 15 cc. of glacial acetic acid, and the mixture was brought to a boiling temperature.

The cold reaction-product was then poured into water, extracted with ether, and the ethereal solution washed with water, dried over calcium chloride, filtered and the ether allowed to evaporate.

The substance remained as an oil, which solidified slowly; it was crystallized from ether and melted at 114° to 115°.

Analysis for carbon and hydrogen gave: Calculated for $C_{14}H_{16}O_6Br$, C, 38.18; H, 3.63. Found, C, 37.89, 38.18; H, 3.90, 3.58.

Benzoate of α-Oxy-β-brom-dihydro-bromisoapiol,

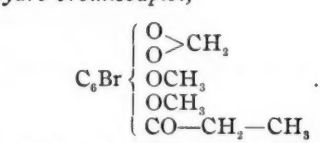


This ester was obtained according to the Einhorn-Hollandt method of preparing benzoyl derivatives.

Five grams of α-oxy-β-brom-dihydro-bromisoapiol were dissolved in 15 cc. of pyridine and treated with 3 grams of benzoyl chloride, which was added gradually. After standing during twenty-four hours, the reaction-mixture was poured into dilute sulphuric acid (1:5), and allowed to remain until the oil, which at first separated, had solidified; the solid was then filtered, washed with dilute acid and water, and crystallized from alcohol. It separates in well-defined crystals, which melt at 117° to 118°.

The following figures were obtained by analysis: Calculated for $C_{19}H_{18}O_6Br_2$, C, 45.41; H, 3.58. Found, C, 45.14, 45.13; H, 3.64, 3.44.

α-Keto-dihydro-bromisoapiol,



Although the ethers of α-oxy-β-brom-dihydro-bromisoapiol are not affected by boiling with concentrated solutions of alcoholic potash or sodium methylate but, in fact, separate from these solutions on cooling and show their original melting-points, nevertheless the free alcohol itself is quite readily changed by the action of hot alcoholic potash. A similar circumstance was noted in the behavior of the derivatives from isosafrol as described above. The compound obtained from the α-oxy-isosafrol derivative is an oil, while that formed from the α-oxy-isoapiol deriv-

ative is a crystalline substance, and analysis seems to indicate that it is a ketone.

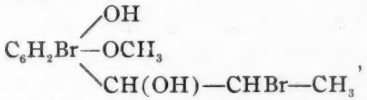
Five grams of α-oxy-β-brom-dihydro-bromisoapiol (m. p. 85° to 86°) were dissolved in 25 cc. of ethyl alcohol, treated with a concentrated solution of 2 grams of potassium hydroxide in alcohol, and boiled in a reflux apparatus for about two hours; at the expiration of this time the separation of potassium bromide was complete and 100 cc. of water were added. Five cc. of hydrochloric acid were then introduced, and the whole boiled for about half an hour. After standing for about twelve hours, a solid substance separated; this was filtered, dried, and crystallized from alcohol. It melts at 128° to 129°.

Another preparation of this substance was made by boiling 23 grams of the α-oxy-compound with a solution of 7 grams of potassium hydroxide in 100 cc. of alcohol, and subsequently treating with water and acid as above-mentioned. The solid product crystallized from alcohol in beautiful, small crystals, which melt at 128° to 129° and are rather sparingly soluble in alcohol.

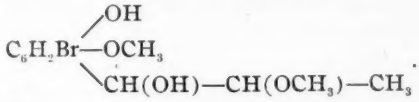
Analysis gave the following results: Calculated for $C_{12}H_{13}O_5Br$, C, 45.42; H, 4.10. Found, C, 45.36, 45.67; H, 4.45, 4.31.

The analysis, therefore, indicates the formula given above. That this compound is a ketone, however, has not been absolutely proved, since our investigation was interrupted at this point; we expect to continue it during the current year. It is exceedingly probable that the substance will prove to be the ketone.

According to Auwers and Müller,[1] α-oxy-β-brom-monobrom-dihydro-isoeugenol,



obtained by the action of aqueous acetone upon monobromisoeugenol dibromide, reacts with sodium methylate, yielding α-oxy-β-methoxy-monobrom-dihydro-isoeugenol,



[1] Auwers and Müller: *Ber. d. chem. Ges.*, **35**, 121.

If a similar reaction had taken place in the treatment of α-β-oxy-brom-dihydro-brom-isoapiol with ethyl alcoholic potash, a compound having the following composition would have resulted:

$$C_6Br\begin{cases} O\\ O>CH_2\\ OCH_3\\ OCH_3\\ CH(OH)-CH(OC_2H_5)-CH_3 \end{cases}$$

This substance contains 46.28 per cent. of carbon and 5.23 per cent. of hydrogen, which are quite different from the figures obtained by analysis. For the present, therefore, we prefer to retain the ketone formula above-mentioned. This line of investigation will be continued and extended to some other substances of a similar constitution.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE NO. 47.—SENT BY H. W. WILEY.]

THE COMPOSITION OF FRESH AND CANNED PINEAPPLES.

BY L. S. MUNSON AND L. M. TOLMAN.

Received January 2, 1903.

THE work undertaken in connection with the investigation of the composition of fresh and canned pineapples consists of the analysis of (1) fresh pineapples from various sources, (2) canned pineapples that were put up under supervision of the Consuls General of the United States at Singapore and Nassau, and (3) commercial samples of canned pineapples.

DESCRIPTION OF SAMPLES.

Of the thirty-eight samples of fresh pineapples examined, twenty-one were from Florida, ten from Cuba, four from Porto Rico, two from the Bahamas and one from Jamaica. The Florida pineapples were largely obtained from representative growers; the Cuban pineapples were nearly all purchased on the market at Havana; the Porto Rican pineapples were obtained from F. D. Gardner, Director of Porto Rican Experiment Station; the Bahama samples were obtained on the market in New York; and the sample from Jamaica was obtained in the Washington market. So far as possible, the samples obtained were the well-ripened fruit, but in some cases they were shipped so far that it was not

practicable to use the thoroughly ripened fruit but such as would stand shipment. Samples 804 to 808 and 818 were secured early in the season and were very green. Their composition shows them to be of inferior quality and therefore they have been excluded from the averages for total solids and for sugars. The first sample of fresh pineapples was received March 4, 1902, and the last sample September 26, 1902, and samples were secured at varying intervals between these dates.

Sixteen samples of canned pineapples were obtained from the Consul-General at Singapore. Of this number, ten were put up in the normal pressed juice of the pineapple without addition of cane-sugar and six were put up in the pressed juice to which cane-sugar had been added. Two samples were obtained from the Consul-General at Nassau, preserved without addition of cane-sugar.

The forty-two samples of commercial canned pineapples came from Singapore, the Straits Settlements and from the Bahamas.

METHODS OF ANALYSIS.

The methods of analysis employed in this work were essentially those given under "Fruits and Fruit Products, Provisional Methods for the Analysis of Foods," Bulletin 65, Bureau of Chemistry. The total solids were determined by drying in a water-oven with asbestos for twenty hours. Solids in the syrup were calculated from the specific gravity, using the table of H. Ellion. Reducing sugars were determined by Meissl's method for invert sugar, and cane-sugar was determined both by the increase in reduction after inversion with hydrochloric acid, and by double polarization. The polarimetric method used was that of the German Official Chemists, and cane-sugar was calculated by the Herzfelt formula,

$$S = \frac{100(A - B)}{141.89 + 0.05B - \frac{T}{2}}.$$

Results by the two methods agreed very closely, especially where the amount of cane-sugar was small. With samples of high content of cane-sugar, the results by the reduction method were less reliable, owing to the influence of the cane-sugar upon the reduction.

While the acids of pineapples are largely citric they are ex-

pressed in this paper as H_2SO_4 for the reason set forth in a previous contribution from this laboratory.[1]

ANALYTICAL DATA.

Table I contains the results of analyses of the fresh pineapples. As will be seen by reference to this table, there is no material difference in composition due to the source of the pineapples; neither does the variety seem to have any influence on the composition. Insoluble solids, ash, acids, and proteïn do not show a wide variation, while on the other hand the samples show a wide difference in the content of sugars. As is well known, the sugars develop very rapidly with the ripening of the fruit. On the other hand the other constituents appear to be present in equally large amounts in the green fruit. Of particular interest is the relative amounts of reducing- and cane-sugars in the fresh fruit. In nearly all cases the cane-sugar is largely in excess of the reducing sugar. The average amount of reducing sugar in all the samples of fresh fruit is 3.91 per cent. while the average amount of cane-sugar is 7.59 per cent.—nearly double the amount of reducing sugar.

Table II contains the results of the analyses of the pineapples canned under direction of the Consuls General at Singapore and Nassau. The samples put up without addition of cane-sugar were preserved in expressed pineapple juice, the amount of juice added being about 30 per cent. of the entire contents of the can. So far as content of total sugars are concerned, therefore, the composition of these canned pineapples should not be materially different from the composition of the normal fresh fruits. Other constituents, especially insoluble solids, will be lowered by the addition of the juice as comparison of Tables I and II shows. While the amount of total sugar is practically the same as in the fresh fruit, the relative proportions of reducing- and cane-sugars are entirely different, due to the inverting action of the organic acids during the processes of canning. In many cases the amount of the cane-sugar remaining is quite small, the average for all the samples being 3.41 per cent. of cane-sugar and 7.99 per cent. of reducing sugars—just the reverse of the condition in the fresh fruit. This condition also holds in the samples put up with addition of cane-sugar, and with the commercial samples.

[1] This Journal, **23**, 347 (1901).

TABLE I.—COMPOSITION OF FRESH PINEAPPLES.

Serial Number.	Variety.	Solids.		Ash.		Acids as H_2SO_4.	Protein (N × 6.25).	Sugars.			Polarizations.		
		Total. Per cent.	Insoluble. Per cent.	Total. Per cent.	Alkalinity as K_2CO_3. Per cent.	Per cent.	Per cent.	Reducing. Per cent.	Cane. Per cent.	Total as Invert. Per cent.	Direct. °V.	Invert. °V.	Temperature. °C.
	FLORIDA:												
571	Spanish red	11.93	1.60	0.438	0.321	0.847	0.406	1.94	5.98	8.24	4.75	— 3.08	22.0
807		8.06[1]	1.55	0.326	0.390	0.366	0.494	1.74[1]	2.96[1]	4.86[1]	1.85	— 2.20	23.4
808		10.19[1]	1.59	0.434	0.497	0.825	0.419	1.44[1]	5.37[1]	7.09[1]	4.35	— 2.30	28.4
1054	Spanish red	16.53	1.48	0.505	0.377	0.509	0.418	5.89	8.71	15.06	6.70	— 4.45	28.0
1055	Porto Rico	12.27	1.48	0.408	0.345	0.307	0.262	4.06	6.49	10.89	5.00	— 3.30	28.0
1056	Egyptian queen	18.86	1.47	0.548	0.377	0.483	0.381	5.20	8.48	14.13	6.85	— 4.01	28.0
1059	Sugar loaf	15.06	1.51	0.356	0.337	....	0.275	3.64	9.12	13.24	8.00	— 3.85	30.0
1060	Spanish red	13.30	1.55	0.361	0.243	....	0.474	4.40	6.48	11.22	5.00	— 3.30	30.0
1061	Abakka	10.78	1.45	0.385	0.292	....	0.331	3.95	4.68	8.88	3.90	— 2.20	30.0
1062	Blood	11.82	1.29	0.446	0.317	....	0.406	3.02	6.13	9.48	5.15	— 2.75	30.0
1063	Spanish red	17.52	1.68	0.428	0.374	....	0.418	4.54	10.20	15.28	8.55	— 4.62	30.0
1064	Smooth cayenne	12.93	1.27	0.378	0.355	0.444	0.400	3.17	7.51	11.08	6.20	— 3.30	27.8
1066	Smooth cayenne	14.85	1.03	0.373	0.322	0.445	0.393	9.75	2.98	12.89	0.20	— 3.63	27.8
1067	Abakka	13.70	1.31	0.349	0.278	0.465	0.419	5.28	6.35	11.97	4.70	— 3.52	27.8
1068	Porto Rico	12.20	1.84	0.526	0.478	0.545	0.569	3.98	6.03	10.33	4.60	— 3.08	27.8
1069	Abakka	12.73	1.27	0.466	0.418	0.620	0.306	4.38	6.22	10.93	4.80	— 3.30	27.8
1070	Spanish red	13.10	1.49	0.464	0.596	0.300	0.475	4.52	6.53	11.40	5.20	— 3.19	27.8
1071	Pernambuco	15.60	1.68	0.487	0.403	0.560	0.406	4.33	8.27	13.03	6.50	— 4.23	27.8
1092	Egyptian queen	13.62	...	0.479	0.459	0.565	0.469	3.62	7.44	11.45	6.40	— 3.08	30.0
1093	Abakka	11.02	1.02	0.395	0.276	0.400	0.338	4.08	4.91	9.45	3.40	— 3.02	25.8
1125	Spanish red	15.25	...	0.401	0.316	0.560	0.494	4.53	8.22	13.19	6.70	— 4.20	21.0
	Average	13.85	1.45	0.421	0.370	0.515	0.407	4.44	6.88	11.69			
	CUBAN:												
572	Spanish red	12.63	1.35	0.272	0.272	0.561	0.406	2.19	6.81	9.36	6.70	— 2.36	21.0
646	Sugar loaf	11.45	1.70	0.324	0.355	0.646	0.206	1.76	6.12	8.20	4.80	— 3.19	23.0

[1] Not included in averages.

TABLE I (continued).—COMPOSITION OF FRESH PINEAPPLES.

Serial Number.	Variety.	Solids. Total. Per cent.	Solids. Insoluble. Per cent.	Ash. Total. Per cent.	Ash. Alkalinity as K_2CO_3. Per cent.	Acids as H_2SO_4. Per cent.	Protein (N × 6.25). Per cent.	Sugars. Reducing. Per cent.	Sugars. Cane. Per cent.	Sugars. Total as invert. Per cent.	Polarizations. Direct. °V.	Polarizations. Invert. °V.	Polarizations. Temperature. °C.
CUBAN :													
647	Spanish red.....	14.12	1.64	0.319	0.328	0.602	0.381	3.00	8.76	12.23	7.10	—4.33	23.0
802	Spanish red.....	13.45	1.63	0.457	0.461	0.670	0.475	2.31	8.23	10.97	7.20	—3.57	27.6
803	Sugar loaf.....	12.67	1.80	0.277	0.223	0.502	0.513	2.76	6.77	9.89	5.90	—3.09	27.6
804		9.13[1]	1.49	0.313	0.353	0.673	0.512	1.34[1]	4.60[1]	6.18[1]	3 50	—2.53	23.4
823	Spanish red.....	17.53	1.54	0.425	0.401	0.511	0.387	3.76	10.48	14.79	9.20	—4.18	28.6
855	Sugar loaf.....	16.53	1.33	0.342	0.360	0.457	0.363	4.55	9.43	14.48	8.10	—4.29	22.6
860	Spanish red.....	15.38	1.81	0.444	0.476	0.624	0.375	2.84	9.65	12.00	8.35	—4.07	25.8
1053	Sugar loaf.....	16.99	1.64	0.296	0.327	0.359	0.357	4.65	9.73	14.89	8.50	—3.90	26.0
	Average.....	14.52	1.59	0.347	0.356	0.561	0.397	3.09	8.44	11.87			
BAHAMA :													
809		14.97	1.52	0.387	0.410	0.798	0.500	2.56	9.18	12.23	8.10	—4.07	28.4
868	Spanish red.....	14.65	1.59	0.408	0.409	0.747	0.462	2.75	8.98	12.21	7.85	—3.74	25.8
	Average.....	14.81	1.56	0.398	0.410	0.772	0.481	2.65	9.08	12.22			
PORTO RICAN :													
805		8.69[1]	1.64	0.416	0.399	0.697	0.431	1.35[1]	3.67[1]	5.22[1]	2.30	—2.36	23.4
818	Cabezona	8.48[1]	1.63	0.332	0.304	0.807	0.519	2.74[1]	3.30[1]	6.22[1]	2.30	—1.92	28.6
819	Pan de Azucar....	14.14	1.69	0.404	0.437	0.524	0.444	2.97	8.22	11.62	7.15	—3.41	28.6
820	Caraquena	17.69	1.83	0.333	0.370	0.838	0.531	4.59	9.97	15.09	8.20	—4.62	28.6
	Average.....	15.91	1.70	0.371	0.378	0.716	0.481	3.78	9.09	13.36			
JAMAICA :													
806		9.23[1]	1.48	0.410	0.410	0.646	0.475	1.28[1]	4.67[1]	6.19[1]	3.55	—2.58	23.4
	Av'ge of all samples	14.17	1.52	0.396	0.370	0.603	0.420	3.91	7.59	11.90			
	Maximum.....	18.86	1.83	0.548	0.596	0.847	0.569	9.75	10.48	15.28			
	Minimum.....	10.78	1.02	0.272	0.223	0.300	0.206	1.76	2.98	8.20			

[1] Not included in averages.

Not included in averages. 0.206 1.76 2.98 8.20

TABLE II.—COMPOSITION OF CANNED PINEAPPLES PUT UP UNDER DIRECTION OF CONSULS GENERAL AT SINGAPORE AND NASSAU.

Serial Number.	Solids. Total. Per cent.	Solids. Insoluble. Per cent.	Ash. Total Per cent.	Ash. Alkalinity as K_2CO_3. Per cent.	Acids as H_2SO_4. Per cent.	Protein ($N \times 6.25$). Per cent.	Sugars. Reducing. Per cent.	Sugars. Cane. Per cent.	Sugars. Total as invert. Per cent.	Polarizations. Direct. °V.	Polarizations. Invert. °V.	Polarizations. Temperature. °C.
Preserved in natural juice without addition of cane-sugar.												
SINGAPORE:												
1103	14.34	1.18	0.447	0.312	0.450	0.566	8.92	3.28	12.38	0.90	—3.30	23.0
1104	14.26	1.31	0.357	0.295	0.466	0.562	9.54	3.34	13.06	0.90	—3.52	23.0
1105	14.41	1.20	0.474	0.338	0.472	0.438	10.96	1.85	12.91	—1.10	—3.52	23.0
1106	13.48	1.15	0.476	0.329	0.490	0.481	9.56	2.44	12.13	0.00	—3.20	23.0
1107	17.44	1.44	0.434	0.352	0.436	0.488	10.56	4.11	14.89	1.60	—3.80	24.4
1108	13.10	1.34	0.309	0.257	0.450	0.506	7.44	4.20	11.86	2.30	—3.20	24.4
1109	10.96	1.16	0.242	0.214	0.250	0.500	5.84	3.85	9.90	2.30	—2.65	24.4
1111	11.70	1.62	0.333	0.301	0.333	0.412	7.53	2.08	9.72	0.30	—2.50	24.4
1112	11.28	0.87	0.330	0.253	0.294	0.444	6.59	3.00	9.83	1.40	—2.60	24.4
1113	12.95	1.83	0.391	0.308	0.299	0.356	7.30	3.17	10.64	1.60	—2.70	24.4
Average..	13.39	1.31	0.379	0.300	0.389	0.475	8.42	3.13	11.73			
NASSAU:												
1013	10.00	1.07	0.257	0.300	0.443	0.250	5.44	2.96	8.55	1.65	—2.09	26.0
1014	16.35	2.18	0.563	0.663	0.711	0.456	6.20	6.61	13.16	4.65	—3.68	26.0
Average..	13.18	1.63	0.410	0.482	0.577	0.403	5.82	4.79	10.86			
Preserved in natural juice with addition of cane-sugar.												
SINGAPORE:												
1114	18.07	1.02	0.370	0.286	0.378	0.412	11.93	4.63	16.70	1.50	—4.50	24.4
1115	18.48	1.38	0.267	0.164	0.202	0.350	12.68	4.88	17.82	1.55	—4.75	24.4
1116	18.15	1.60	0.460	0.329	0.260	0.400	7.51	8.82	16.80	7.00	—4.30	24.4
1117	18.61	2.06	0.505	0.336	0.284	0.456	9.02	7.83	17.26	6.50	—4.60	24.4
1118	19.11	1.25	0.450	0.328	0.417	0.450	15.39	2.41	17.93	1.65	—4.80	24.4
1119	16.61	1.33	0.334	0.234	0.378	0.375	13.28	2.28	17.93	0.20	—4.25	24.4
Average..	18.17	1.44	0.398	0.280	0.320	0.407	11.63	5.14	17.41			

TABLE III.—COMPOSITION OF CANNED PINEAPPLES—COMMERCIAL SAMPLES.

	Specific gravity of syrup.	Solids in syrup. Per cent.	Solids. Total. Per cent.	Solids. Insoluble. Per cent.	Ash. Total. Per cent.	Ash. Alkalinity as K_2CO_3. Per cent.	Acids as H_2SO_4. Per cent.	Protein ($N \times 6.25$). Per cent.	Sugars. Reducing. Per cent.	Sugars. Cane. Per cent.	Sugars. Total as invert. Per cent.	Polarizations. Direct. °V.	Polarizations. Invert. °V.
SINGAPORE—(Twenty-one samples):													
Average...	1.0869	20.15	21.03	1.17	0.284	0.225	0.269	0.461	9.61	7.88	17.86	5.01	—5.22
Maximum.	1.1112	25.30	26.84	1.67	0.363	0.282	0.433	0.569	13.73	16.48	25.10	15.00	—6.60
Minimum.	1.0744	18.18	18.45	0.92	0.208	0.164	0.156	0.388	7.05	4.34	14.87	0.00	—4.40
STRAITS SETTLEMENTS—(Ten samples):													
Average...	1.0868	20.08	21.04	1.08	0.259	0.225	0.259	0.466	10.51	7.54	18.45	4.53	—5.37
Maximum.	1.0998	22.86	24.28	1.27	0.322	0.324	0.323	0.569	15.18	10.65	21.94	7.70	—6.27
Minimum.	1.0717	16.79	17.32	0.91	0.224	0.138	0.171	0.394	7.70	4.70	14.55	0.00	—4.20
BAHAMAS—(Eleven samples):													
Average...	....	....	14.13	1.39	0.381	0.304	0.558	0.335	7.96	2.78	9.98	0.56	—3.31
Maximum.	....	....	26.78	2.51	0.497	0.388	1.176	0.456	12.84	9.05	22.37	4.70	—7.15
Minimum.	....	....	8.54	0.88	0.222	0.199	0.220	0.200	5.55	0.53	6.33	—2.40	—1.32

Table III contains the results of analyses of forty-two samples of canned pineapples from Singapore, the Straits Settlements and the Bahamas. It is apparent from the high content of sugars that practically all of the canned pineapples from Singapore and the Straits Settlements are preserved with addition of cane-sugar. On the other hand, the analyses indicate that but few of the samples from the Bahamas have had any addition of cane-sugar.

A study of the data contained in the foregoing tables fails to bear out the common supposition that the pineapples grown upon or near the equator contain more sugar than those grown at some distance farther north, and in fact, the normal content of sugar in pineapples grown in Florida differs so little from that of pineapples grown at Singapore that the difference is practically negligible.

It may not be out of place to state at this point, that these investigations were undertaken in the Bureau of Chemistry at the request of the Secretary of the Treasury for the purpose of establishing a basis of classification for imported pineapples for the guidance of the appraisers. Since the classification of these bodies for dutiable purposes depends upon the answer to the question of whether or not sugar has been added during the process of preserving, it was necessary, first to establish the normal content of sugar in the pineapples. It is evident, from inspection of the analyses, that since the normal pineapples contain a large quantity of cane-sugar, the mere presence of this substance would be no evidence whatever of its artificial addition. It is further evident, that if a syrup containing practically the same quantity of sugar as the natural syrup of the pineapple were added, it would be quite impossible, by a mere determination of the sugar present, to detect the addition. The only guide in this case would be to determine the relation of the sugar present to the total insoluble matters of the pineapple.

If, on the other hand, a syrup rich in sugar were added in preserving, it would be easily detected by the increase in the percentage of sugar in the contents of the can.

In looking over the literature accessible to us relating to the analysis of pineapples, at the commencement of these investigations, we were surprised to find that no paper has been published on this subject except one by Buignet in "Les Sucres," published by Maquenne (Paris, 1900).

The average content of sugar found by Buignet, *viz.*, 13.9 per cent. as invert sugar is not materially different from the amount found in these investigations.

THE EFFECT OF MOISTURE ON THE AVAILABILITY OF DEHYDRATED PHOSPHATE OF ALUMINA.

BY FRED. W. MORSE.

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THE author has from time to time encountered samples of phosphatic material, which have borne the name of concentrated phosphate, and which really are dehydrated phosphate of alumina and iron.

Such materials usually contain approximately 45 per cent of phosphoric anhydride, of which more than 0.5, and sometimes as much as 0.8, will dissolve in a neutral solution of ammonium citrate.

The phosphatic mineral from which this fertilizer is made, is obtained principally from the islands of Redonda and Grand Connetable in the West Indies, and is a hydrated phosphate of alumina and iron.

The author has made several analyses of the mineral from the former island, and a number of analyses have been published by Shepard,[1] Tate,[2] and Hitchcock,[3] while only one analysis made by Andouard,[4] is yet known to him of the latter phosphate. The composition of the two phosphates is very similar. The phosphoric anhydride ranges from 35 per cent. to 39 per cent. in cargoes and as high as 43 per cent. in the richest specimens.

The water contained in the mineral is nearly proportional to the phosphoric anhydride, the ratio averaging $2P_2O_5$ to $9H_2O$. Two analyses including Andouard's give $10H_2O$, while two analyses have been as low as $8H_2O$. The proportion of Al_2O_3 to Fe_2O_3 is irregular; usually the former exceeds the latter, especially in the richer specimens.

The process of preparing the mineral for use as a fertilizer, was patented by the late Stephen L. Goodale,[5] who described the prin-

[1] *Am. J. Sci.*, **47**, 428.
[2] *J. Soc. Chem. Ind.*, **8**, 570.
[3] *Bull. Geol. Soc. Am.*, **2**, 6-9.
[4] *Ann. Agronom.*, **21**, 171.
[5] "Conversion of Hydrous Phosphates of Alumina and Iron." Monograph, 1893.

ciples of his method in a pamphlet from which the following is quoted.

"The sample properly prepared by reduction to fineness and removal of dust, is gradually heated in a properly equipped receptacle. Elevation of temperature proceeds regularly to about 100° C., at which point a halt ensues, usually attended by a fall of several degrees. During this halt, heat is apparently absorbed; when the halt ceases, elevation of temperature again proceeds regularly to a point near 150°, when another notable halt occurs; when this ceases, elevation proceeds without interruption to full dehydration and beyond, if permitted. This point may be determined by seasonably exposing a cold surface to the orifice where escaping vapor may be deposited as dew. Application of the test should begin at least as soon as 250° or 260° is reached; the point of complete dehydration varies in samples of differing composition, sometimes as low as 275°, rarely beyond 330°, usually near 325° C."

In speaking of the results of the process, Goodale further says: "To attain these fully, the heat must reach the definite, critical point of complete dehydration. If only one-fourth, one-half or three-fourths be expelled, corresponding enhancement in value does not accompany such expulsion. Moreover, if elevation of temperature goes beyond the critical point, change also goes on toward non-solubility, so that most skilful watchfulness is indispensable to avoid loss."

Although this dehydration results in a high percentage of available phosphoric acid as measured by its solubility in ammonium citrate, the use of the calcined phosphate in experiments with plants, has not shown itself to possess any such degree of availability when applied to the soil.

This fact has been especially demonstrated by several series of pot experiments made at the Main Experiment Station,[1] with twelve different kinds of plants; and by three successive years of field experiments at the Rhode Island Experiment Station[2] with a rotation of corn, oats and grass.

It was further noted in the Maine experiments, for which the dehydrated Redonda phosphate was prepared in the Station laboratory, that the availability of the substance in ammonium citrate

[1] Maine Agr. Expt. Sta. Reports (1893), pp. 10-20; (1895), pp. 10-20; (1898), pp. 64-74.
[2] R. I. Agr. Expt. Sta. Reports (1894), pp. 122-128; (1896), pp. 327-343.

decreased on standing, and that it was necessary to prepare a fresh quantity of phosphate for each series of comparisons, which suggested that the dehydrated phosphate reverts to the hydrated condition in the soil. Goodale mentions in his pamphlet that, under certain conditions, the phosphate retrogrades; but does not give any particulars beyond intimating that it is due to overheating.

In order to get more knowledge of the nature of the dehydrated phosphate, and of its availability, a series of experiments was carried out in the spring of 1900, to determine the amount of dehydration at different temperatures, with the resultant solubility in ammonium citrate of the phosphate, and to see if the dehydrated mineral would revert in the presence of moisture.

In this series of experiments, the author was assisted by Mr. R. H. Shaw, now of the Kansas Experiment Station. For material there was used ground Redonda phosphate obtained in 1891 from Mr. Goodale for field experiments.

The mineral was analyzed with the following results: Water at low red heat, 21.33 per cent.; phosphoric anhydride, 35.92 per cent.

The temperatures selected for dehydration were those mentioned by Goodale, *viz.*, 100°, 150°, 250° and 325° C., and in addition 560° and 830° C., or the fusing points of borax and sodium carbonate respectively.

The estimation of water at 100° was made by heating the mineral in wide weighing bottles, in an air-bath, at a temperature of 100° to 105° C. The material was weighed at intervals of two hours, and the weight at the end of the fourth hour was practically the same as that at the end of the sixth.

At the approximate temperature of 830° the determination was conducted by heating in a platinum crucible over a Bunsen flame, and ascertaining the loss in weight, as in the foregoing experiment. The temperature was reached by adjusting the lamp flame so that anhydrous sodium carbonate was brought to a quiet fusion in a platinum crucible. Then, without disturbing the lamp, the sodium carbonate crucible was removed and another platinum crucible of the same size containing the phosphate was placed in the triangle.

At the intermediate temperatures, the water was not only determined by the loss in weight of the material, but also by the gain

in weight of a calcium chloride tube into which the vapor was passed.

The apparatus was arranged similarly to that for a combustion in a current of air or oxygen, and consisted of a combustion tube connected at one end with a drying tower and at the other end with a weighed U-tube containing calcium chloride.

The charge of phosphate was placed in a porcelain boat, inserted in the combustion tube, and pushed to the middle. For the temperatures of 150°, 250°, and 325°, a tube oven was used instead of a combustion furnace. For that at 560° a special furnace was constructed of a piece of magnesium-asbestos steam-pipe covering, a little shorter than the combustion tube. A rectangular opening was cut in the middle of the lower half-section long enough to admit the tops of three Bunsen burners placed in a line. The tube was supported above the burners by a strip of asbestos board, and when the upper half section was in place, the flames played around the tube as in a combustion furnace. In order to determine the degree of heat sustained by the mineral, a porcelain boat containing anhydrous borax was inserted in the combustion tube along with the boat containing the phosphate, the latter being next to the calcium chloride tube. The borax was maintained at the stage of fusion, which could be observed by removing the upper half section of the improvised furnace.

Determinations of the loss in weight at the temperature of fusing borax were also made by heating in a platinum crucible in exactly the way used with sodium carbonate.

In the tube oven, the temperatures of 150° and 250° were determined by thermometers as in heating sealed tubes; but since in this operation, a current of air was slowly drawn through the tube, the temperature of the mineral would be somewhat below that registered by the thermometers, which were therefore allowed to run about 10° above the stated temperatures before readjusting the lamps.

For the approximate temperature of 325°, the thermometer registered 350°; but powdered potassium nitrate contained in a boat placed in the tube reached only the stage of incipient fusion.

The three salts used for determining temperatures were of Kahlbaum's sealed brand of C. P. chemicals, and showed no impurities excepting with the spectroscope.

Richards[1] gives them the following melting-points: Potassium nitrate, 339° C.; sodium biborate, 561° C.; sodium carbonate, 830° C.

In the tube method, at the temperatures of 325° and 560° the water was expelled from the mineral quickly and condensed around the end of the combustion tube next the calcium chloride tube, requiring several hours for its removal by the current of air drawn through the apparatus, since it was necessary to pass the air slowly in order to insure complete absorption.

For the absorption method, it was found necessary to use smaller charges than for the methods depending solely on loss of weight. The effectiveness of the drying-tower was demonstrated by blank determinations, and that of the U-tube by connecting a second calcium chloride tube and weighing it separately. The results are given in the following table.

PERCENTAGES OF WATER EXPELLED AT DIFFERENT TEMPERATURES.

Temperature. °C.	Per cent. by loss.	Per cent. by absorption.
100	18.14	....
150	19.72	19.93
250	20.32	20.26
325	20.71	20.78
560	21.34	20.98
560	21.32	after heating 15 min. in crucible.
830	21.57	" " 5 " " "
830	21.54	" " 15 " " "
830	21.63	" " 30 " " "
830	21.45	" " 60 " " "

The results corroborate the statements of Goodale regarding the expulsion of water at 100° and 150° but do not show complete dehydration at 325°.

The slightly lower results obtained by absorption at 560° were probably due to incomplete removal of water from the combustion tube; but might also be due to the destruction of organic matter which can hardly fail to be present, owing to the fact that the porous phosphate is more or less penetrated by the roots of grasses and cacti, and Andouard in his analysis of Grand Connetable phosphate reports traces of carbon dioxide.

In determining the availability of the phosphate, the official neutral solution of ammonium citrate[2] was used; but the citrate-

[1] *Am. Chem. J.*, **20**, 704.

[2] "Methods of Analysis, Association of Official Agricultural Chemists," Bull. 46, Bur. of Chem., U. S. Dept. Agr., p. 11.

soluble phosphoric acid was determined directly, instead of indirectly as in the official method. This was done because in all previous work with this particular phosphate, it was found impossible to prevent the finest particles of mineral running through any paper filter that would permit a ready passage of the citrate solution. Ross' method[1] was therefore selected, which is based on digesting the filtrate of citrate-soluble phosphoric acid with sulphuric acid and oxidizing agents, as in the Kjeldahl method for nitrogen, after which the molybdate solution is used as usual. Of course, this method gives somewhat lower results than the indirect method; but this is not due to incomplete recovery of the phosphoric acid, which was repeatedly verified. The method of procedure then, was to digest 1 gram of the mineral in 100 cc. of neutral ammonium citrate, filter through an asbestos felt with the aid of a pump, digest aliquot parts of the filtered solution after Ross' method, and determine the phosphoric acid as usual. By the use of an asbestos felt, it was possible to get a clear filtrate and to remove the citrate solution quickly from the mineral. The availability of the phosphate at the different stages of dehydration was found to be as follows:

Undehydrated	2.08 per cent. P_2O_5
Heated to 100°	19.64 " " "
" " 150°	27.25 " " "
" " 250°	32.76 " " "
" " 325°	31.53 " " "
" " 560°	32.65 " " "
" " 830° 15′	11.35 " " "
" " 830° 90′	2.53 " " "

These results show, that to get the highest degree of availability, it is necessary to remove practically all of the water; but they do not confirm the statement that a continuation of the heat beyond 325° lowers the solubility, since at 560° the mineral underwent the heating for from six to eight hours while the water was being aspirated from the tube. The high temperature required to fuse sodium carbonate produces, however, a marked decrease in solubility, and this is intensified by prolonging the heating.

The effect of exposure to a moist atmosphere was determined by placing the dehydrated phosphate under a bell-jar, in an atmosphere saturated with moisture from an open dish containing water. The phosphate was weighed in a porcelain boat placed

[1] Bull. 38, Bur. of Chem., U. S. Dept. Agr., p. 16.

inside a weighing-tube, and the boat was exposed under the bell-jar, until it had reached equilibrium with respect to moisture, before the dehydrated mineral was weighed into it. The charges used were small, in order to expose as much surface as possible to the action of the moist atmosphere.

The different degrees of dehydration, which were compared, were those obtained by heating to 250°, 325°, 560°, and 830° respectively. The results obtained were unlooked for and of much interest.

Phosphate dehydrated at 250°; charge, 0.2965 gram.

Water absorbed in 24 hours, 0.0565 gram.
" " " 72 " 0.0690 "
" " " 120 " 0.0705 "

Total water absorbed, 23.78 per cent. of charge taken

Phosphate dehydrated at 325°; charge, 0.2200 gram.

Water absorbed in 24 hours, 0.0425 gram.
" " " 72 " 0.0485 "
" " " 120 " 0.0495 "

Total water absorbed, 22.50 per cent. of charge taken.

Phosphate dehydrated at 560°; charge, 0.6495 gram.

Water absorbed in 24 hours, 0.0415 gram.
" " " 48 " 0.0585 "
" " " 96 " 0.0605 "

Total water absorbed, 9.32 per cent. of charge taken.

Phosphate dehydrated by heating fifteen minutes at 830°; charge, 0.4730 gram.

Water absorbed in 24 hours, 0.0065 gram.
" " " 48 " 0.0095 "

Total water absorbed, 2.00 per cent. of charge taken.

The moistened phosphate was next transferred to an ammonium citrate solution and its availability determined by the same method that was employed after dehydration. As the charges of phosphate of the temperatures 250° and 325° were so small, they were combined for the determination of available acid. The quantity of citrate solution was reduced to 50 cc. in all these cases, since the charges were approximately only 0.5 gram each.

The availability of the four grades of phosphate was now found to be as follows:

250° and 325°, 19.30 per cent. P_2O_5 in dehydrated phosphate.
560° 29.76 " " " " " "
830° 7.09 " " " " " "

The experiment was repeated with the phosphates dehydrated at 325° and 560°.

Phosphate dehydrated at 325°; charges (*a*), 0.4160 gram; (*b*), 0.5330 gram.

Water absorbed in 75 hours, (*a*) 0.0900 gram; (*b*) 0.1140 gram.
" " " 96 " " 0.0950 " " 0.1200 "
" " " 240 " " 0.1090 " " 0.1460 "
Total water absorbed, (*a*), 26.20 per cent.; (*b*), 27.39 per cent. of charge taken.

Phosphate dehydrated at 560°; charges (*a*), 0.4450 gram; (*b*), 0.6820.

Water absorbed in 24 hours, (*a*), 0.0370 gram; (*b*), 0.0540 gram.
" " " 48 " " 0.0480 " " 0.0660 "
" " " 120 " " 0.0580 " " 0.0800 "
" " " 240 " " 0.0710 " " weight lost.
Total water absorbed in 120 hours, (*a*), 13.04 per cent.; (*b*), 11.72 per cent.
Absorbed in 240 hours, (*a*), 15.95 per cent.

For the estimation of available phosphoric acid the duplicate charges of each grade were combined, making an approximate charge of 1 gram for each grade, and 100 cc. of citrate solution were used. The availability in this trial was respectively:

325° 11.54 per cent. P_2O_5 in dehydrated phosphate.
560° 27.70 " " " " " "

Having on hand about 200 pounds of the dehydrated phosphate obtained in 1891, which had been stored, since then, in the basement of the laboratory exposed in an open barrel, it was tested for availability in ammonium citrate in order to determine its keeping qualities. In 1891 this lot contained 46.85 per cent. total and 21.91 per cent. available phosphoric acid, and but a trace of moisture. In 1900 a new analysis yielded 10.98 per cent. water; 41.95 per cent. total phosphoric acid and 14.60 per cent. available. The decrease in total phosphoric acid is proportional to the absorption of water, while the drop in available is far in excess of such hydration.

Some of the material was next exposed to a moist atmosphere for eight days, in which time it gained 9.42 per cent. of its weight, and on determining the available phosphoric acid, it was found to have fallen to 11.31 per cent. of the original charge.

The phosphates dehydrated at 325° and 560°, respectively, were next subjected to the action of water saturated with carbon di-

oxide, and its effect was also tried on the undehydrated mineral. One gram of material was taken in each instance and placed in a flask with 200 cc. of water. Carbon dioxide was passed into the water in each flask, during thirty to sixty minutes, twice a day for six days, and the flask was shaken two or three times during its passage. The gas was prepared from sodium bicarbonate and sulphuric acid, to avoid any acid vapors, and was washed before it entered the flask. At the end of the period, an aliquot part of clear liquid was taken from each flask and tested for phosphoric acid. The amount appeared so slight in each case, that no attempt was made to determine the proportion for each grade of material; but the filtrates from the three were combined and then concentrated by evaporation, after which the phosphoric acid was determined as the average for the lot, and found to be 0.31 per cent. of the charges taken.

Each residue was next digested with the ammonium citrate solution and the amount of available phosphoric acid estimated, which was as follows:

Undehydrated	0.69	per cent. of charge taken.
Dehydrated at 325°	6.67	" " " " "
" " 560°	24.95	" " " " "

By these different series of experiments, the rapid deterioration of the dehydrated phosphate with respect to its available phosphoric acid, is clearly shown in the case of the material prepared according to Goodale's process, and the claim is contradicted that heating beyond 325° is injurious. The results show without exception that the temperature at which borax fuses is not too high for good results, and that the phosphate, after being heated to that point, is more permanently soluble, and less apt to again become hydrated. Whether it would be more available to plants than those lots subjected to lower temperatures, cannot be told without vegetation tests.

NEW HAMPSHIRE COLLEGE AGRICULTURAL
EXPERIMENT STATION.

CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 75.]

NORMAL HEPTYL THIOCYANATE AND SOME NEW ALKYL ESTERS OF DITHIOCARBAMIC ACID.

BY MARSTON TAYLOR BOGERT.

Received January 7, 1903.

SEVERAL years ago, in connection with certain investigations then under way, the writer had occasion to prepare the substances described in this paper. As there is but little likelihood of this line of work being resumed, it seems advisable to record the properties of these new compounds for the information of other workers in this field, particularly since J. v. Braun, in his recent article on the dithiourethanes,[1] calls attention to the fact that only two (ethyl and isopropyl) alkyl esters of unsubstituted dithiocarbamic acid are mentioned in the literature.

Normal Heptyl Thiocyanate, $C_7H_{15}SCN$.—Normal heptyl bromide was prepared by the action of bromine and amorphous phosphorus upon normal heptyl alcohol, the bromide being driven out of the crude reaction product by a rapid current of steam. The separated bromide was washed with water, with sodium carbonate solution, with water again, dried with calcium chloride, treated with cold concentrated sulphuric acid to remove unchanged heptyl alcohol, washed, dried again and distilled. As thus prepared, normal heptyl bromide forms a colorless oil, boiling at 175.5°-177.5° (uncorr.) at 765 mm., and volatile with steam. In concentrated alcoholic solution this bromide rapidly transposes with potassium thiocyanate, the reaction being complete in about half an hour, if conducted at the boiling-point of the solution. The separated thiocyanate, washed and dried, distils at 234°-236° (uncorr.). Rectified under diminished pressure, the pure substance is obtained as a colorless mobile oil of peculiar but not unpleasant odor, boiling-point 136° (corr.) at 28 mm.; sp. gr. at 20°, 0.92.

Normal Heptyl Sulphonic Acid, $C_7H_{15}SO_3H$.—The thiocyanate was oxidized by heating with moderately strong nitric acid. After the evaporation of the nitric acid, the syrupy residue was taken up with water, excess of barium carbonate added, the mixture boiled, and filtered hot. The barium salt of the sulphonic acid crystallized from the filtrate, on cooling, in pearly white scales, only moder-

[1] *Ber. d. chem. Ges.*, **35**, 3369 (1902).

ately soluble in cold water or in cold 95 per cent. alcohol, and containing no water of crystallization. Spring and Winssinger,[1] by the action of chlorine upon the normal heptyl sulphoxide, obtained a mixture which they believed contained barium heptyl sulphonate, but they did not separate the mixture or obtain the barium salt in question in a pure state.

Normal Heptyl Dithiocarbamate, $H_2NCSSC_7H_{15}$.—Normal heptyl thiocyanate was treated with hydrogen sulphide at 100°, the hydrogen sulphide being driven in against a pressure of 7 inches of mercury. In the course of six to ten hours, glassy prisms of the dithiocarbamic ester separated. Recrystallized from a mixture of naphtha and carbon bisulphide, large glassy prisms of soapy feel were obtained, melting at 65°, and easily soluble in methyl alcohol, chloroform, benzene, acetone and carbon bisulphide, difficultly soluble in naphtha or kerosene.

Normal Propyl Dithiocarbamate, $H_2NCSSC_3H_7$, prepared from normal propyl thiocyanate and hydrogen sulphide in a similar manner, crystallizes from a mixture of naphtha and carbon bisulphide, in large colorless prisms, melting-point 57°, insoluble in water, very easily soluble in methyl, ethyl or isoamyl alcohols, in benzene, toluene, acetone, chloroform or carbon bisulphide, easily soluble in hot naphtha or kerosene but on cooling tends to separate as an oil. Through the kindness of Dr. Austin F. Rogers, of the Mineralogical Department of this University, the crystals were measured, with the following results:

Crystals—tabular, parallel to basal pinacoid.

Monoclinic—$a : b : c = 0.8536 : 1 : 0.9447$. $\beta = 77° 7'$.

Observed forms—*c* (001), *a* (100), *m* (110), *t* (012), *q* (011).

			Measured.	Calculated.
mm'''	(110∧1̄10)	(7)	100° 28′	.....
cm	(001∧110)	(6)	80° 8′	.....
cq	(001∧011)	(6)	43° 38.5′	.....
c'm	(00ī∧110)	(3)	99° 53.5′	99° 52′
qq'''	(011∧01ī)	(4)	94° 44′	94° 43′
ct	(011∧012)	(3)	24° 45′	24° 43′

Cleavage—perfect, parallel to *c*; imperfect, fibrous parallel to *a*.

Isoamyl Dithiocarbamate, $H_2NCSSC_5H_{11}$, from amyl thiocyanate and hydrogen sulphide, under similar conditions, crystallizes from a mixture of carbon bisulphide and naphtha in glassy

[1] *Bull. Soc. Chim.*, **49**, 72.

micaceous scales, melting-point 51.5°, easily soluble in methyl or ethyl alcohols, in chloroform, carbon bisulphide, benzene, acetone, very difficultly soluble in boiling water, difficultly soluble in cold naphtha or kerosene but easily soluble in these solvents when boiling.

NOTE.—Since writing the above, an article has appeared by Delépine,[1] in which he describes the methyl, ethyl, normal and isopropyl, benzyl and *p*-nitrobenzyl dithiocarbamates, and gives the melting-point of the normal propyl compound as 58°.

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THE FREEZING-POINTS OF DILUTE SOLUTIONS.

BY THEODORE WILLIAM RICHARDS.

Received January 9, 1903.

THE difficulties which attend the accurate determination of the freezing-points of dilute solutions, according to the ordinary method of procedure, are well known. A brief perusal of the work of Jones,[2] Loomis,[3] Nernst and Abegg,[4] and Raoult[5] is enough to convince even a hasty reader that besides the common errors of thermometry, and of quantitative work in general, the process is especially complicated by the slowness with which the equilibrium is attained. This complication results in either supercooling or superheating, according as the system is being cooled or warmed. Nernst and Abegg performed a valuable service in calling attention to this danger, and the latter of the two, as well as Loomis and Raoult, carried out a few accurate determinations guarding especially against it. Unfortunately, however, their precautions were so elaborate that few experiments were made, and the difficulty seems to have deterred other workers in the same field.

It is easy to see that another method may be used, a method which overcomes the chief difficulty in a simpler manner; and the

[1] *Bull. Soc. Chim.*, **3**, 29-30, 48 (1903).

[2] Jones: *Ztschr. phys. Chem.*, **11**, 110 and 529; **12**, 623 (1893).

[3] Loomis: *Wied. Ann.*, **51**, 500 (1894); also *Ztschr. phys. Chem.*, **32**, 578 (1900); **37**, 497 (1901).

[4] Nernst and Abegg: *Ztschr. phys. Chem.*, **15**, 681 (1894); also Abegg: *Ibid.*, **20**, 207 (1898).

[5] Raoul : *Compt. Rend.*, **125**, 751 (1897).

present paper has as its object the brief presentation of this simpler method.

As has been said, the prime difficulty is the delay in attaining the true equilibrium. Since this equilibrium is one between two phases, it can be adjusted only on the surface between the two. The speed is therefore proportional to the extent of surface. In order then to avoid the danger of superheating or supercooling, one must have as much ice present as possible, instead of as little as possible. Nothing could be easier than the carrying out of the process under these new conditions. It is true that the solution surrounding the ice must be analyzed, but this may often be done volumetrically or simply by evaporating portions to dryness, and the labor thus involved is vastly less than that involved in the older method.[1]

While the Beckmann apparatus may be thus used with a large excess of ice, fairly accurate results may be obtained more simply as follows. A tall beaker of at least half a liter capacity is filled with finely cracked ice. In many cases a slight impurity present in the ice will not cause a serious error, unless the impurity present is such as to influence the degree of dissociation of the substance to be studied, or chemically to combine with it. It is important in this case, however, that the water at first surrounding the ice should have the same amount of impurity as the ice itself; hence, it is well to use a melted sample of the same material for this purpose. The beaker is surrounded by a protection of wool or cotton several centimeters thick, in order to delay the melting. The temperature of the melting ice is then taken by means of a deeply immersed accurate thermometer, allowing the zero point to become constant. A small portion of the substance to be studied, dissolved in a small volume of the same water, is added and the mixture is stirred with a pipette until the temperature has become approximately constant, and then the pipette is freed from the little cold liquid which it contains and quickly used to draw out its volume of liquid from the immediate neighborhood of the thermometer bulb. The thermometer, which of course should be gently tapped before each reading, remains surprisingly constant during this process, since the slow melting takes place only on the sides and top of the beaker, and the diffusion through the inter-

[1] Roloff thus analyzed concentrated solutions. *Ztschr. phys. Chem.*, **18**, 572 (1895). A. A. Noyes has kindly suggested to me the use of electrical conductivity as a convenient means of analyzing the solution without withdrawing it.

stices of the ice is too slow to have an important effect. If this withdrawn pipetteful measured 10 cc. and is titrated by means of an N/10 solution, the number of cubic centimeters of titrating solution divided by 100 gives at once the approximate equivalent normality of the freezing solution. For the greatest accuracy, of course, allowance should be made for the contraction of the glass and of the solution at the low temperature; but for approximate results these complications are not necessary. By means of this very simple apparatus it is easy to obtain a depression of half a degree within half a per cent. of its true value.

When it is desired to obtain a result accurate to within less than the thousandth of a degree, greater precautions of all kinds must be taken. The thermometer must become seasoned to the low temperature by remaining for hours, or even for days, in melting ice, in order that the slow rise of the zero point due to the slow internal adjustment of the glass may have ceased; the pressure due to the atmosphere and the height of the liquid should be carefully observed, since the bulb is compressible; the thermometer should be carefully calibrated with reference to the international hydrogen scale; the inflow and outflow of heat should be reduced to a minimum, and pure ice must be used. No thermometer can ever give an accurate reading of a temperature which is not constant for many minutes, because the thermometer possesses heat capacity, and its temperature must therefore inevitably lag behind that of its changing environment.[1]

The inflow or outflow of heat may easily be prevented by immersing the experimental vessel in a mixture possessing a temperature, within a few hundredths of a degree, the same as that inside. Such a mixture is very easily made with pounded ice and small portions of any soluble salt, added in solution until an auxiliary thermometer graduated into tenths of a degree indicates a sufficient approach to the temperature desired.[2] An air jacket, such as is used in Beckmann's apparatus, is an advantage, if it can be entirely immersed in this bath, but if it allows the convection of warm air it is rather a disadvantage than an advantage. A Dewar flask might answer well. For results of the greatest accuracy, the vessels should all be large. If these principles are heeded, almost any form of apparatus will yield good results.

[1] This error greatly complicates the correction for cooling in calorimetric experiments, but is usually disregarded.

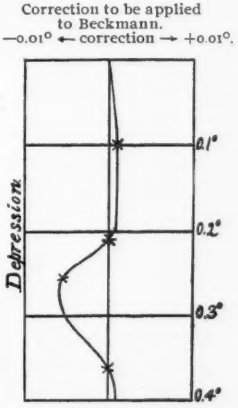
[2] Nernst and Abegg used constant temperature-baths of this kind (*loc. cit.*).

The determinations recorded below were conducted as follows: A Jena flask holding somewhat over a liter, was fitted with a rubber stopper containing three holes. One of these received the thermometer (which was arranged so as to come no nearer than a centimeter to the bottom of the flask), another a short fine funnel-tube for admitting the salt solution, and the third a short, wide glass tube large enough to admit the long stem of a 20 cc. pipette. This pipette was used for withdrawing portions of the solution, its point was always allowed to remain several minutes in the ice, and the liquid remaining in it was always expelled, before it was filled by suction. If the flask has not a wide neck, the stem of the pipette should be slightly bent just below the bulb, otherwise this bulb collides with the projecting thermometer stem.

During an experiment, the flask was somewhat more than half-filled with carefully washed, cracked ice, and at first contained enough ice-water to reach about a centimeter above the top of the thermometer bulb,—enough to render the pieces of ice easily mobile. The flask was then immersed in a large bath of similar cracked ice, and was packed in cotton wool and cloth and left with the thermometer stem projecting for forty-eight hours. In this time, the arbitrary zero point of the thermometer rose from a minimum of 3.805 to 3.820, where it remained during the experiments, so long as there was no large change in the pressure on the bulb. When the zero point had been established, successive portions of potassium chloride solution were added, and the corresponding positions of the mercury thermometer were read after suitable agitation and delay. The contents of the flask were easily mixed by removing it from the ice-bath and giving it a rotary motion. As already suggested, the ice-bath was provided with an essentially isotonic solution by stirring in dilute salt solution until an auxiliary thermometer indicated about the same depression in the outside bath as that exhibited by the accurate thermometer within the flask. Constancy was usually reached within five or six minutes from the introduction of the dissolved substance. The successive change in concentration might be most conveniently effected by adding successive portions of the solution, having the same volumes as that previously removed by the pipette. If the solution were cooled before its introduction, the amount of ice would remain nearly constant, although hardly constant enough to dispense with the analysis of the solution.

The thermometer used in these experiments was one of the Beckmann type, made by F. O. R. Götze in 1895, divided into hundredths of a degree. In order to make certain of the value of its degree, it was compared with thermometer Baudin 15275, which was made and standardized with the greatest precision by the Bureau International des Poids et Mesures for this purpose.[1] The following table and accompanying diagram gives the results of this comparison, which was made after both thermometers had been in ice for a long time. The bath in which they were compared consisted of properly protected and stirred ice fragments immersed in suitably dilute solutions of salt. The readings were made with an accurate Geneva microscope-micrometer.

Beckmann thermometer.	Standard thermometer (corrected).
3.820°	+0.107°
3.817°	+0.104°
3.718°	+0.004°
3.604°	−0.110°
3.559°	−0.148°
3.456°	−0.257°
3.100°	−0.617°



This table was verified by measuring lengths of short mercury columns in various places, a process which indicated a narrow place in the bore between 3.60° and 3.50°; but nevertheless this question of calibration is the most serious difficulty in the whole matter. Its import is so great as to make the present paper a preliminary one rather than a final statement of the depressions corresponding to definite solutions. According to the method described there is no difficulty in attaining a great degree of constancy in the thermometer readings; but to determine the true temperature from these readings is a far more difficult problem. The thermometer bulb was not allowed to become warm throughout the series of experiments, for fear of changing the settled structure of the cold glass. The correction for the projecting thread of the thermometer was eliminated by the constancy of the conditions.

Potassium chloride was chosen as the substance to be studied in order to facilitate comparison with the work of other experi-

[1] See *Proc. Am. Acad.*, **38**, 434 (1902).

menters, who have nearly always used it as one of their substances. The specimen employed was precipitated by hydrochloric acid from a pure solution, and thoroughly dried. The amounts present in the respective solutions were determined by a modified form of Vohard's method, titrating the excess of standard silver nitrate with sulphocyanate, after filtering off the precipitated silver chloride, which otherwise disturbs the reaction by its solubility. The solutions were standardized in a similar way with pure fused potassium chloride. Since the solutions were N/5, and the instruments were accurate,[1] the reading for the silver nitrate divided by 100 gives at once the normality of the freezing solutions.

Below is given a table of data and results which are enough to indicate the satisfactory constancy of the readings. An hour elapsed between the first and third experiments, as well as between the eighth and tenth. The atmospheric and hydrostatic pressure on the thermometer bulb were essentially constant.

No. of experiment.	Concentration of solution (normal standard).	Observed depression.	Corrected depression.	Molar depression.
1	0.1256	0.433°		
2	0.1261	0.433°	0.433°	3.42
3	0.1258	0.432°		
	0.1258	0.433°		
4	0.0944	0.330°		
5	0.0944	0.330°	0.328°	3.48
	0.0944	0.330°		
6	0.0386	0.136°		
7	0.0388	0.136°	0.137°	3.52
	0.0387	0.136°		
8	0.0311	0.112°		
9	0.0309	0.111°	0.112°	3.59
10	0.0307	0.111°		
	0.0309	0.111°		

These results are near those of other experimenters, who needed much more labor than that expended in the present case. For example, Abegg found, for the concentrations 0.0469 and 0.0354, molecular depressions of 3.47 and 3.50 respectively, results but slightly lower than those given above.

[1] The most important burette, that used for the silver nitrate, was unusually fine in bore and in graduation, having been marked only after careful preliminary calibration by the author.

While the study of a single electrolyte furnishes too meager a basis for extended theoretical conclusions, especially when the possible inaccuracy of the thermometer introduces a wide range of possible error, it may not be out of place to compare these molar depressions with those calculated from the conductivity. In order to make this comparison, it would be necessary to know the average molar depression caused by a non-electrolyte with an equal degree of accuracy. For the present the value, 186° taken from the average of many previous investigations, is sufficiently accurate. On this basis the degrees of dissociation of the four solutions whose depressions are recorded above are easily calculated as 0.84, 0.87, 0.89, and 0.93 respectively.

The most accurate data concerning the electrolytic conductivity of aqueous solutions are perhaps those of Kohlrausch and Maltby,[1] but unfortunately these do not apply in the present case, since the temperature used was 18°, not 0°. Next to these comes the work of Whetham,[2] who worked with very great care at the required temperature. He found the equivalent conductivity of potassium chloride to be 75.2 when diluted to 33 liters per mol, and to attain a maximum of 80.7 when diluted to 2000 liters. This leads to the value 0.93 for the degree of dissociation of the former solution, a solution which corresponds exactly to the last one named in the preceding paragraph.

The agreement between these two results (0.93 according to both the depression of the freezing-point and the electrical conductivity) is closer than would be expected from the possible errors of the results compared. So far as it goes, therefore, it is satisfactory to the adherent of the modern theory of solution; but many more comparable results with other substances should be obtained before the subject is allowed to drop.

The constancy of the thermometric readings obtained in this way from mixtures of ice with dilute solutions suggests the availability of such mixtures as a means of calibrating thermometers below the freezing-point. If an accurate curve were plotted, comparing the normality of the solution with the actual depression of the freezing-point, all that would be necessary in order to determine the error of a given point in a thermometer would be to place

[1] *Wiss. Abh. phys. tech. Reichsanstalt*, **3**, 157 (1900).

[2] *Ztschr. phys. Chem.*, **33**, 344 (1900). The work of Déguisne at 2° indicates essentially the same value as that of Whetham. (Inaug. Diss., Strassburg, 1895.) Unfortunately Déguisne has not presented his data, but has concealed them in quadratic equations.

it in pure ice and then to stir into the ice an increasing amount of the standard solute until the desired point on the thermometer was reached and maintained. An analysis of the commingled solution, with the help of the curve, would then at once give the temperature which the thermometer ought to have recorded, and hence the error of the given point on the thermometer. Hydrochloric acid would perhaps be the best substance for this purpose, since it is easily prepared in a pure state and may be determined volumetrically in a variety of ways.

Such a means of calibrating thermometers would be theoretically as exact as any other, for according to the phase rule, with two components, four conditions must be fixed in order to fix a point. In the present case, the four conditions would be two phases, pressure, and the concentration of the dissolved substance. The experience gained in the trials recorded above seems to indicate that this method is practically feasible as well as theoretically sound, and in the near future more accurate data concerning the true course of some such curve will be obtained here.

Besides this, it is my object to study with the help of the new method a number of electrolytes and non-electrolytes with all possible accuracy, using a platinum resistance thermometer.

SUMMARY.

It is pointed out that in the presence of much ice the equilibrium concerned in the freezing-point of solutions is obtained with great speed and convenience. Several forms of apparatus are suggested for this determination, and results are given, showing that the plan is capable of practical execution. The exactness seems to be so great that the method may be of use in standardizing thermometers. The few data found are consistent with the hypothesis of ionization.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 68.]

DERIVATIVES OF NEW COMPLEX INORGANIC ACIDS.[1]

BY ALLEN ROGERS.

Received January 2, 1903.

THE splendid research work upon complex inorganic acids, by Dr. Wolcott Gibbs, has brought to view numerous classes of most

[1] From the author's thesis for the Ph.D. degree presented in June, 1902.

interesting bodies. So full of interest have they been that other students have ventured to enter the field and, as might be expected, have extended the limits of our knowledge in this particular domain of chemical science. Yet, the end seems not reached, for a glance at the ammonium vanadico-phospho-tungstate described by Smith and Exner[1] discloses again a new class or series of complex inorganic acids, in which there exists a triple complex acid. Wolcott Gibbs described somewhat similar bodies in which, however, the vanadium oxide present was the dioxide and not the trioxide as is the case with the compound isolated by Smith and Exner. To reproduce the body obtained by these chemists and gain further insight into its constitution and deportment was the primary purpose of the present investigation which has resulted in the discovery of a number of analogous derivatives, a description of which will now be given.

AMMONIUM PHOSPHO-VANADIO-TUNGSTATE,

$$13(NH_4)_2O.2P_2O_5.8V_2O_5.34WO_3 + 86H_2O.$$

Preparation.—In the preparation of this salt various amounts of ammonium phosphate, ammonium vanadate, and ammonium tungstate were boiled together for six hours. The solution, after filtration, was evaporated and allowed to crystallize. The crystals formed in every case were identical in physical appearance and, as will be seen later, had the same chemical composition.

The best results were obtained when 1 gram of ammonium phosphate, 15 grams of ammonium tungstate, 3 grams of ammonium vanadate, 20 cc. of ammonium hydroxide, and 700 cc. of water were brought together, in a liter flask, and boiled for six hours. At first the solution was colorless, but soon changed to yellow and then to red. At this point the ammonium tungstate dissolved very rapidly, and the solution became much darker in color. The slight residue was filtered off, and the filtrate evaporated to a specific gravity of 1.115. On standing over night, the salt separated. The mother-liquor was again evaporated, and a second crop of crystals was obtained.

Properties.—The product of the above procedure gave dark red-colored crystals, which were octahedra and cubes in form; very soluble in cold and hot water; insoluble in alcohol, ether, carbon disulphide, benzene, and nitrobenzene. No change was produced

[1] This Journal, **24**, 573.

when the crystals, reduced to a fine powder, were treated with dilute nitric or hydrochloric acid. Strong hydrochloric acid gave a yellow precipitate, with the evolution of chlorine, on boiling. Strong nitric acid produced a yellow precipitate, which dissolved on the addition of water. With ammonium hydroxide, there was no change. Caustic potash or soda gave a yellow precipitate, which dissolved on boiling, with the evolution of ammonia. Mercurous nitrate formed a yellow precipitate, which turned red when dry; insoluble in boiling water or an excess of the reagent; but rendered soluble by a few drops of nitric acid. This precipitate was found to be the mercury salt of phospho-vanadio-tungstic acid, and from it the acid was prepared. A discussion of this acid, and its salts with the heavy metals, is not within the scope of this paper. It may not, however, be out of place to give some of the principal points at this time. Starting with ammonium phospho-vanadio-tungstate, the silver or mercury (better silver) salt was precipitated. This precipitate was washed, and dried; or, in most cases, was placed in a flask with a few drops of nitric acid and brought to boiling. When the solution was complete, it was filtered and evaporated to a small volume, and, on standing over night, crystals of silver phospho-vanadio-tungstate were deposited. These crystals were removed and dissolved in water, and to the solution hydrochloric acid was added, a few drops at a time, until all of the silver was precipitated. The silver chloride was filtered off and the filtrate evaporated on the water-bath to a small volume. From this solution the acid was deposited in dark red, octahedral crystals. A solution of this acid gave the same reaction with the heavy metals as those produced by the ammonium salt. With ammonium phospho-vanadio-tungstate, and also with phospho-vanadio-tungstic acid the precipitates formed were found to be due to the deposition of metallic derivatives of the above-mentioned acid.

To come back to the ammonium salt again: It was found that copper nitrate produced no change in the solution; but when ammoniacal copper nitrate was added, a red precipitate was formed, insoluble in boiling water, but dissolving very readily when a few drops of nitric acid were added. Ammoniacal cadmium chloride gave an orange-colored precipitate, slightly soluble in boiling water; but very soluble in nitric acid. Stannous chloride gave a gray precipitate, rapidly taking on a blue tint. Am-

moniacal cobalt nitrate produced a greenish gray precipitate, which turned red when dried. Zinc acetate gave a yellow precipitate quite soluble in boiling water. Barium chloride, in an ammoniacal solution, gave a light yellow precipitate, which remained insoluble on boiling, but dissolved readily when a little nitric acid was added.

Method of Analysis.—The methods proposed by Gibbs[1] and Friedheim[2] could not be used in the analysis of the black crystals obtained by Smith and Exner; neither were they applicable to this salt. After trying various means the following was found to give very satisfactory results:

The air-dried salt was reduced to a fine powder, and a known quantity introduced into a tared crucible. It was heated gently at first, then the temperature was increased, and continued until constant weight was obtained. The loss represented the water and ammonium oxide. The residue was boiled with dilute nitric acid in which the vanadium pentoxide and phosphorus pentoxide dissolved, leaving the tungsten trioxide insoluble. After standing several hours, the precipitate was filtered off. It was washed with a little water containing nitric acid, dried, ignited, and weighed as tungsten trioxide. The tungsten trioxide nearly always held some vanadium pentoxide which was removed by gently heating in a current of hydrochloric acid gas. The filtrate from the tungsten trioxide was evaporated to dryness in a weighed porcelain crucible on the water-bath, and then gently heated over the flame. The mass fused. In this way the combined weight of the phosphorus pentoxide and vanadium pentoxide was determined. The fusion was taken up with water containing a little nitric acid, in which it dissolved readily on warming. The phosphorus pentoxide was thrown out with a magnesia mixture. The ammonium magnesium phosphate was dissolved in dilute nitric acid, and reprecipitated by addition of ammonium hydroxide, when it came down free from vanadium. The vanadium pentoxide was then determined by difference. To make sure, however, that the difference was vanadium pentoxide, in a number of cases, vanadium was thrown out from the filtrate, with concentrated ammonium chloride and alcohol. On ignition of the ammonium vanadate so found vanadium pentoxide was produced, which in

[1] *Am. Chem. J.*, **1**, 217; **2**, 217, 281; **3**, 119; **4**, 377; **5**, 391; **7**, 313, 392.
[2] *Ber. d. chem. Ges.*, (1890), pp. 353, 1503, 1530, 2600.

each case corresponded to the amount obtained by difference. The ammonium oxide was ascertained by boiling a new portion of the salt with caustic potash, the liberated ammonia being collected in a standard solution of hydrochloric acid, and the excess titrated with ammonium hydroxide. The ammonium oxide found by this means was subtracted from the ammonium oxide and the water determined by ignition. The difference gave the true water content.

Result of Analysis.—The percentages as given below are for salts prepared from eight different combinations. It shows, therefore, that the same compound was always produced.

	Theory.	Found.							
$(NH_4)_2O$....	5.71	5.72	5.77	5.77	5.57	5.87	5.59	5.59	5.89
P_2O_5.....	2.39	2.32	2.60	2.60	2.43	2.52	2.33	2.51	2.25
V_2O_5.....	12.28	12.09	12.25	11.91	12.50	12.23	12.03	11.68	12.07
WO_3.....	66.55	66.33	66.39	66.32	66.35	66.44	66.41	66.39	66.35
H_2O	13.07	13.17	12.78	13.16	13.09	12.97	13.63	13.77	12.84
	100.00	99.63	99.89	99.76	99.94	100.03	99.99	99.94	99.40

SILVER PHOSPHO-VANADIO-TUNGSTATE,

$$13Ag_2O.2P_2O_5.8V_2O_5.33WO_3 + 41H_2O.$$

When silver nitrate is added to a solution of ammonium phospho-vanadio-tungstate a brick-red precipitate is formed, which is soluble to some extent in water, and is completely dissolved by water to which a few drops of nitric acid are added. The compound is obtained pure by washing with water until the wash-water gives no test for nitric acid. The following method of analysis may be employed:

Method of Analysis.—Have the precipitate dried at 70° for one hour after being air-dried, in the state of a fine powder, and heat a weighed amount of it to dull redness; the loss will give the amount of water of crystallization. Another portion is dissolved in water containing a few drops of nitric acid; then hydrochloric acid is added to remove the silver as silver chloride. The filtrate from the silver chloride is evaporated to dryness in a weighed crucible with a little nitric acid, and the weight, after strongly heating, represents the combined tungsten trioxide, phosphorus pentoxide and vanadium pentoxide. This mass is then digested with dilute nitric acid, and the tungsten trioxide filtered off and weighed; as this trioxide may contain a little

vanadium pentoxide, it is always necessary to heat in a current of hydrochloric acid to remove the last trace of vanadium. The filtrate from the tungsten trioxide is treated with ammonium hydroxide to alkaline reaction, and the magnesia mixture added to throw out the phosphoric acid. As the magnesium ammonium phosphate also contains some vanadium, it is necessary to dissolve it and reprecipitate. The amount of vanadium pentoxide is determined by difference, *i. e.*, the phosphorus pentoxide plus the tungsten trioxide, subtracted from the total phosphorus pentoxide, vanadium pentoxide, and tungsten trioxide.

RESULTS OF ANALYSIS.

	Theory.	Found.						
Ag_2O	22.93	22.81	22.66	21.91	22.44	23.17	22.83	23.17
P_2O_5.....	2.15	2.18	2.14	2.12	2.19	2.01	2.21	2.08
V_2O_5.....	11.09	11.23	11.09	13.31	12.17	11.17	11.21	11.25
WO_3.....	58.22	58.01	58.11	57.56	57.66	58.02	58.17	58.05
H_2O	5.61	5.59	5.51	5.73	5.65	5.53	5.57	5.47
	100.00	99.82	99.51	100.63	100.11	99.90	99.99	99.97

In this case, a mean of the results is taken for the derivation of the formula and corresponds very closely with that found for the ammonium salt. The difference of 1 molecule of tungsten trioxide may be eliminated if a number of the results under the analysis of the ammonium salt had been chosen for the calculation instead of a mean of all them.

It will be observed that red-colored salts were obtained by the methods pursued in the preceding paragraphs, while the ammonium salt described by Smith and Exner had a deep black color. Later, it was discovered that this color was caused by the reduction of the vanadium to a lower oxide; therefore, the following salt was prepared:

AMMONIUM PHOSPHO-VANADICO-TUNGSTATE,

$$15(NH_4)_2O.2P_2O_5.6V_2O_3.44WO_3 + 106H_2O.$$

Preparation.—The salt was obtained by bringing together 1 gram of ammonium phosphate, 15 grams of ammonium tungstate, 1.1 grams of vanadium trioxide (prepared by heating 1.6 grams of ammonium vanadate with strong hydrochloric acid, and evaporating to dryness on a water-bath), 25 cc. of ammonium hydroxide with 700 cc. of water, and boiling the mixture for six hours. By

this means a black-colored solution resulted, which was evaporated to a specific gravity of 1.030 and allowed to stand over night in a cool place. The crystals obtained had a deposit of ammonium chloride on the surface. This was removed by washing them with a little cold water, and the product was finally dried on filter-paper.

Properties.—The salt as prepared in the above manner gave black crystals with octahedral and cubic habit, the octahedral being far in excess and truncated by the faces of the cubes. The compound was soluble in water; insoluble in alcohol, ether or benzene. Dilute nitric acid produced a slight change in color on boiling. The same thing occurred with dilute hydrochloric acid. Strong hydrochloric acid produced a yellow precipitate, but without the evolution of chlorine on boiling. Concentrated nitric acid gave a yellow precipitate, which dissolved on adding water. Ammonium hydroxide produced no change. Potassium hydroxide gave a yellow precipitate, which partly dissolved on boiling, at the same time giving off ammonia, while a black residue remained. Mercurous nitrate gave a yellow precipitate, which remained insoluble on boiling, but dissolved on adding a little nitric acid. Silver nitrate gave a greenish black precipitate. Barium chloride produced a gray precipitate which dissolved when heated, but separated again on cooling. The composition of the salt was very much like that obtained from the mother-liquor of ammonium paratungstate by Smith and Exner, but differed from it in some of its properties.

Method of Analysis.—The same method was applied as for the first salt, except that the resulting vanadium pentoxide was calculated into vanadium trioxide, and the difference added to the percentage of water of crystallization.

RESULT OF ANALYSIS.

	Theory.	Found.				
$(NH_4)_2O$	5.53	5.44	5.44	5.32	5.32	5.35
P_2O_5	2.02	1.94	2.03	1.84	1.94	1.94
V_2O_3	6.39	6.34	6.34	6.32	6.06	6.26
WO_3	72.50	72.34	72.23	72.55	72.99	72.52
H_2O	13.56	13.60	13.59	13.43	13.69	13.55
	100.00	99.66	99.63	99.46	100.00	99.62

AMMONIUM PHOSPHORICO-VANADIO-TUNGSTATE.

It was thought that this salt would result when ammonium

phosphite, ammonium tungstate and ammonium vanadate were brought together. Such, however, was not the case. The compound produced proved to be ammonium phospho-vanadico-tungstate. This, no doubt, was due to the reducing action of phosphorus trioxide on vanadium pentoxide.

AMMONIUM PHOSPHORICO-VANADICO-TUNGSTATE,

$$14(NH_4)_2O.2P_2O_3.7V_2O_3.31WO_3 + 78H_2O.$$

Preparation.—The next thought to present itself for consideration was to see if a salt could be prepared having the phosphorus and vanadium both in the lower state of oxidation. To accomplish this, 1.5 grams of ammonium phosphite, 1 gram of vanadium trioxide, 20 grams of ammonium tungstate, 25 cc. of ammonium hydroxide, and 700 cc. of water were brought together. After boiling for five hours, the black-colored solution was filtered, and evaporated to about one-fourth of its original volume.

Properties.—The resulting black octahedral crystals were soluble in water; insoluble in alcohol, ether, carbon disulphide, and benzene. The action of dilute or strong nitric or hydrochloric acid, mercurous nitrate, or even silver nitrate was the same as in the previous salt. Barium chloride produced no change when first added to the solution; on standing, an olive-green precipitate was formed.

Method of Analysis.—The same method was used as in former cases; except that a few drops of nitric acid were added to the mass after ignition. The excess of acid was driven off by warming in the water-bath, and the crucible again strongly heated. The resulting vanadium pentoxide and phosphorus pentoxide were calculated to vanadium trioxide and phosphorus trioxide, the difference being added to the percentage of water.

These seem to be all of the possible combinations in this series; that is, in which we have one base united to one oxide of each of the three acid-forming elements.

RESULT OF ANALYSIS.

	Theory.	Found.				
$(NH_4)_2O$	6.85	6.80	6.86	6.86	6.75	6.75
P_2O_3	2.07	2.03	2.02	1.94	2.11	2.00
V_2O_3	9.89	10.08	10.21	10.06	9.91	9.38
WO_3	67.98	67.91	67.73	66.77	68.11	68.02
H_2O	13.21	12.93	12.45	12.77	12.74	13.74
	100.00	99.75	99.54	99.40	99.62	99.89

It has been demonstrated that phosphorus, vanadium, and tungsten combine to form a series of complex inorganic acids. These acids have also been shown to be stable bodies, and capable of giving salts with many basic radicals. The reactions obtained with the heavy metals show a difference from those produced by salts of any of the individual members. The conclusion drawn from these reactions and the constant composition given by analysis is that the compounds under consideration are definite bodies, and not mixtures of phosphates, vanadates, and tungstates.

In the same group with phosphorus is arsenic. This element has many properties in common with phosphorus. The question arose: Can we have a series of compounds in which arsenic takes the place of the phosphorus? The idea appeared to be plausible. Ammonium arsenate and ammonium arsenite were, therefore, substituted for the corresponding phosphorus salt and the following series of compounds prepared:

Ammonium arseno-vanadio-tungstate.
Ammonium arseno-vanadico-tungstate, and
Ammonium arsenico-vanadico-tungstate.

AMMONIUM ARSENO-VANADIO-TUNGSTATE,

$$18(NH_4)_2O.2As_2O_5.13V_2O_5.39WO_3 + 88H_2O.$$

Preparation.—To 700 cc. of water, made alkaline with 15 cc. of ammonium hydroxide, 1 gram of ammonium arsenate, 15 grams of ammonium tungstate and 1 gram of ammonium vanadate were added. The mixture was heated to boiling and maintained at that temperature for five hours. The solution was, at first, colorless, but soon changed to yellow, and then to red, but the red was not as intense as in the case of the phospho-salt. The filtered solution was evaporated and on standing over night the salt separated.

Properties.—The small octahedral crystals which were formed above were soluble in water, but insoluble in organic solvents. Dilute hydrochloric acid or nitric acid was without action. When boiled with strong hydrochloric acid, chlorine was evolved, and a yellow precipitate produced; on further boiling, the precipitate dissolved, but reappeared when the solution had become cold, or on the addition of water. Mercurous nitrate gave a yellow precipitate, which remained insoluble on boiling, but dissolved when nitric acid was added. From this precipitate it seems probable

that the acid can be obtained. Silver nitrate gave a red precipitate, soluble in boiling water, hastened by a drop or two of nitric acid. Lead acetate, ammoniacal copper nitrate or other salts of the heavy metals gave precipitates, which resembled those obtained from the corresponding phospho-compound. As far as studied, these precipitates were derivatives of arseno-vanadio-tungstic acid. A more complete study, however, may bring out many interesting facts. But as the purpose of this paper is to point to the different possibilities, rather than to go too much into detail, we will leave the thought, and, as time goes on, and more work is carried out in this line of investigation, let us hope that the gaps may be filled, and that the completed structure may have its proper place in the great family of inorganic compounds.

Method of Analysis.—The same procedure was employed as for the phospho-salts.

RESULT OF ANALYSIS.

	Theory.	Found.				
$(NH_4)_2O$	6.51	6.63	6.63	6.73	6.73	6.68
As_2O_5	3.18	3.17	2.94	3.11	3.11	3.08
V_2O_5	16.39	16.80	16.75	16.22	16.26	16.51
WO_3	62.95	62.70	62.75	62.81	62.86	62.80
H_2O	10.97	10.54	10.51	10.83	10.58	10.61
	100.00	99.84	99.58	99.70	99.54	99.68

AMMONIUM ARSENO-VANADICO-TUNGSTATE,

$$17(NH_4)_2O.2As_2O_5.14\tfrac{1}{2}V_2O_3.29WO_3 + 98H_2O.$$

Preparation.—In the synthesis of this body 1 gram of ammonium arsenate, 15 grams of ammonium tungstate, 1 gram of vanadium trioxide, 25 cc. of ammonium hydroxide and 700 cc. of water were boiled for five hours. The filtered solution was evaporated on the water-bath to about one-half of the original volume. It was then removed to a cool place and allowed to stand over night. The crystals were usually covered with a deposit of ammonium chloride which was removed by a little cold water. The crystals from the mother-liquor were often mixed with other salts. In order, therefore, to get concordant results, crystals of the first crop were submitted to analysis.

Properties.—The salt, as prepared above, consisted of black octahedral forms, sparingly soluble in cold water; readily soluble in boiling water; insoluble in alcohol, ether, benzene, carbon di-

sulphide, chloroform, acetone, acetic anhydride, nitrobenzene, and aniline. Dilute nitric acid produced a change in color from black to red. Dilute hydrochloric acid changed the color likewise when it was boiled with this reagent. Strong nitric acid gave a yellow precipitate, which dissolved on the addition of water. Strong hydrochloric acid gave a yellow precipitate. Mercurous nitrate produced a red precipitate, which remained insoluble on boiling, but dissolved when nitric acid was added. Silver nitrate gave a dark green precipitate. An attempt was made to get the acid from this salt, but through the action of nitric acid an oxidation took place, the result being that arseno-vanadio-tungstic acid was produced. It may be possible, however, to liberate arseno-vanadico-tungstic acid by some other method, and from the acid so obtained many new compounds would result.

Method of Analysis.—The method used for the corresponding phospho-salt was employed in this case.

RESULT OF ANALYSIS.

	Theory.	Found.			
$(NH_4)_2O$	7.34	7.26	7.25	7.29	7.29
As_2O_5	3.82	3.77	3.80	3.77	3.62
V_2O_3	18.06	18.11	18.06	17.33	18.17
WO_3	56.12	56.04	55.99	56.04	56.07
H_2O	14.66	14.41	14.46	14.35	14.40
	100.00	99.59	99.56	99.78	99.55

AMMONIUM ARSENICO-VANADIO-TUNGSTATE.

By analogy, the production of this compound was looked upon as improbable. A mixture, however, of ammonium arsenite, ammonium vanadate and ammonium tungstate was boiled for six hours. The solution turned dark in color, and finally became black, due to the formation of ammonium arseno-vanadico-tungstate. It may be possible, however, under proper conditions to obtain this salt, as the reduction is not so marked as in the case of the ammonium phosphorico-vanadio-tungstate.

AMMONIUM ARSENICO-VANADICO-TUNGSTATE,

$$16(NH_4)_2O.5As_2O_3.15V_2O_3.26WO_3 + 101H_2O.$$

Preparation.—In the production of this compound the same line of thought suggested itself as in case of the corresponding phosphorico-salt. If vanadium could unite with arsenic as arsenic

pentoxide in two ways, it seemed probable that it would unite with it as arsenic trioxide. A number of different combinations were tried to determine this, but on boiling together 1 gram of arsenic trioxide, 12 grams of ammonium tungstate, 1 gram of vanadium trioxide, 50 cc. of ammonia and 700 cc. of water, the best results were obtained. After boiling for five hours, the solution was evaporated to about one-half its original volume. On standing in a cool place for twenty-four hours the salt separated.

Properties.—Black octahedral crystals sparingly soluble in cold water, which dissolved readily when boiled. Dilute nitric acid produced a change in color. Strong hydrochloric acid gave a yellow precipitate. Nitric acid gave a yellow precipitate, which remained insoluble on boiling, but dissolved when water was added. Silver nitrate produced a greenish black precipitate, which readily dissolved on the addition of a little nitric acid. Barium chloride gave a gray precipitate, insoluble on boiling; readily soluble in dilute nitric acid.

RESULT OF ANALYSIS.

	Theory.	Found.		
$(NH_4)_2O$	6.96	7.02	7.02	7.02
As_2O_3	8.28	8.26	8.12	8.41
V_2O_3	18.83	18.97	18.95	18.99
WO_3	50.70	50.69	50.57	50.71
H_2O	15.23	15.18	15.23	15.13
	100.00	100.12	99.89	100.26

AMMONIUM PHOSPHO-VANADIO-VANADICO-TUNGSTATE,

$$14(NH_4)_2O.2P_2O_5.7V_2O_5.3V_2O_3.27WO_3 + 66H_2O.$$

Preparation.—After proving that compounds could exist in which the phosphorus and vanadium were in either state of oxidation, the question arose: Can a compound be prepared in which the same element is present in both conditions? It seemed possible, as Gibbs has shown, that such bodies can exist. It remained to determine if the presence of phosphorus would have any effect on the combination. For the preparation of this salt, 1 gram of ammonium phosphate, 1 gram of ammonium vanadate, 1 gram of vanadium trioxide, 16 grams of ammonium tungstate, 30 cc. of ammonium hydroxide, and 700 cc. of water were used. This mixture was boiled for five hours. The solution was then filtered, and the greenish black liquid was evaporated on the water-bath;

when reduced to about one-half of the original volume it was set aside to crystallize.

Properties.—The product obtained from the above solution gave greenish black octahedral crystals, which were sparingly soluble in cold water, but dissolved on boiling. Dilute nitric acid or hydrochloric acid changed the color to red. Strong hydrochloric acid decomposed it, with the evolution of chlorine. Strong nitric acid gave off fumes of nitrogen peroxide, while a green precipitate was produced, which dissolved on addition of water. Mercurous nitrate gave a yellow precipitate, which remained insoluble on boiling; but dissolved when nitric acid was added. Barium chloride produced a greenish gray precipitate, which dissolved on boiling, but reappeared when cooled.

Method of Analysis.—The procedure was, for the most part, the same as in former cases. The total vanadium was determined as vanadium pentoxide. A separate portion was boiled with hydrochloric acid, when vanadium pentoxide was reduced to vanadium dioxide, with the elimination of chlorine. The evolved gas was conducted into a solution of potassium iodide, and the liberated iodine titrated with standard sodium thiosulphate.

$$I_2 : V_2O_5 :: \text{Amt. of } Na_2S_2O_3 \times \text{Strength} : x.$$

The true amount of vanadium pentoxide was thus ascertained. This result subtracted from the total vanadium gave the vanadium pentoxide from which the vanadium trioxide was calculated.

RESULT OF ANALYSIS.

	Theory.	Found.		
$(NH_4)_2O$	7.14	7.34	7.23	7.23
P_2O_5	2.78	2.66	2.74	2.57
V_2O_5	12.50	12.62	12.68	12.68
V_2O_3	4.41	4.33	4.36	4.17
WO_3	61.48	61.28	61.40	61.15
H_2O	11.69	11.64	11.55	11.80
	100.00	99.87	99.96	99.60

AMMONIUM ARSENO-VANADO-VANADICO-TUNGSTATE,

$$17(NH_4)_2O.2As_2O_5.7V_2O_5.4V_2O_3.32WO_3 + 73H_2O.$$

Preparation.—From the readiness with which arsenic entered into combination in the salts already studied, it seemed likely that a body related to the one just described could be prepared by introducing arsenic pentoxide in place of phosphorus pentoxide.

This was accomplished by using 1 gram of ammonium arsenate, 1 gram of ammonium vanadate, 1 gram of vanadium trioxide, 16 grams of ammonium tungstate, 30 cc. of ammonium hydroxide, and 700 cc. of water.

The boiling was continued for four hours. The solution, which was greenish black in color, was evaporated on the water-bath until it had reached about one-half its original volume. It was then filtered while hot; and being placed in a crystallization dish, was set aside to cool. In most cases, at the end of twenty-four hours the salt had separated. The mother-liquor was again evaporated and a second crop of crystals was obtained. The yield of salt was much larger in these vanadio-vanadico-compounds than in the vanadico salt.

Properties.—The body produced in this case gave crystals which were black in color, and belonged to the same class as in former cases. The deposit of ammonium chloride was removed by washing with cold water. The solubility was the same as usual. Dilute nitric or hydrochloric acid changed the color of the solution from black to light red. Strong hydrochloric acid decomposed the salt, giving off chlorine, and producing a bright yellow precipitate of the hydrated oxide. Nitric acid gave an orange-colored precipitate, soluble on the addition of water. Mercurous nitrate, and barium chloride gave olive-green colored precipitates insoluble in boiling water, but soluble on the addition of a few drops of nitric acid.

RESULT OF ANALYSIS.

	Theory.	Found.		
$(NH_4)_2O$	7.41	7.42	7.42	7.42
As_2O_5	3.84	3.71	3.79	3.63
V_2O_5	10.65	10.36	10.26	10.26
V_2O_3	5.02	5.26	5.32	5.27
WO_3	62.09	62.12	62.04	62.20
H_2O.....	10.99	10.94	10.95	10. 5
	100.00	99.81	99.78	99.73

It was impossible to introduce phosphorus or arsenic in two conditions, at the same time having vanadium present as vanadium pentoxide, the reason for this being that a reduction of the vanadium pentoxide took place. At the same time the phosphorus or arsenic was oxidized to the higher condition. Were it not for the strong reducing action of arsenic trioxide and phosphorus

trioxide we could expect to obtain six new salts in the above manner. As a matter of fact, it was only possible to get two.

AMMONIUM PHOSPHO-ARSENO-VANADIO-TUNGSTATE,

$$82(NH_4)_2O.12P_2O_5.3As_2O_5.52V_2O_5.201WO_3 + 567H_2O.$$

Preparation.—After having obtained salts, in which the vanadium was present in two states of oxidation, the question arose: Is it possible to have phosphorus and arsenic together with the vanadium? It remained to ascertain if the arsenic and phosphorus would unite, or if the phosphorus would produce one body, and the arsenic another. This could only be determined by analysis of the first and second crop of crystals.

In the preparation of the salt, 1 gram of ammonium phosphate, 1 gram of ammonium arsenate, 2 grams of ammonium vanadate, 16 grams of ammonium tungstate, 20 cc. of ammonium hydroxide, and 700 cc. of water were boiled for six hours. The solution, which had taken on a deep red color, was filtered while hot. It was then evaporated to one-fourth of its original volume, and on standing over night, the salt was deposited. A second crop of crystals was obtained from the mother-liquor. These were placed in a separate bottle, for the reason given above.

Properties.—The salt so prepared consisted of dark red crystals which were octahedral in form, very soluble in warm water, but insoluble in organic solvents. Dilute nitric or hydrochloric acid was without action. Strong hydrochloric acid produced a yellow precipitate with the evolution of chlorine. Strong nitric acid gave a precipitate, soluble on the addition of water. Mercurous nitrate gave an orange-colored precipitate, insoluble on boiling, but rendered soluble by the addition of a few drops of nitric acid. Barium chloride produced no change in the cold, but on warming, a light yellow precipitate came down.

Method of Analysis.—The salt was treated as in former cases, except that the magnesium pyrophosphate and magnesium pyroarsenate, after weighing, were dissolved in hydrochloric acid and hydrogen sulphide passed through the solution to throw out the arsenic. Thus phosphorus pentoxide was determined by throwing out the magnesium pyrophosphate again, giving the arsenic and phosphorus either direct or by difference.

RESULT OF ANALYSIS.

	Theory.	Found.			
$(NH_4)_2O$	5.82	5.81	5.79	5.79	5.84
P_2O_5	2.32	2.24	2.26	2.22	....
As_2O_5	0.98	0.98	1.00	0.81	....
V_2O_5	12.95	13.07	13.05	13.09	....
WO_3	63.98	63.85	63.86	63.67	63.91
H_2O	13.95	13.87	13.88	13.85	....
	100.00	99.82	99.84	99.35	

AMMONIUM PHOSPHO-ARSENO-VANADICO-TUNGSTATE,

$$88(NH_4)_2O.12P_2O_5.2As_2O_5.69V_2O_3.148WO_3 + 484H_2O.$$

Preparation.—Having made the combination of phosphorus pentoxide, arsenic pentoxide, and vanadium pentoxide, the next step was to introduce the vanadium as the trioxide. For this purpose 1 gram of ammonium phosphate, 1 gram of ammonium arsenate, 2 grams of vanadium trioxide, 16 grams of ammonium tungstate, 30 cc. of ammonium hydroxide and 700 cc. of water were boiled for four hours. The greenish black solution was filtered while hot. It was then evaporated to about one-half of its original volume, and on standing over night, in a cool place, the salt separated. The second crop of crystals was contaminated with impurities, and could not be used for analysis.

Properties.—Greenish black, octahedral crystals, soluble in water, insoluble in alcohol or ether. Dilute nitric or hydrochloric acid was without action. Strong hydrochloric acid gave a red solution, with only a slight cloudiness being formed; on addition of water a heavy yellow precipitate came down. The precipitate produced by nitric acid dissolved on the addition of water. Mercurous nitrate and barium chloride produced yellow precipitates, which remained insoluble on boiling, but dissolved when a little nitric acid was added.

RESULT OF ANALYSIS.

	Theory.	Found.		
$(NH_4)_2O$	7.59	7.58	7.52	7.58
P_2O_5	2.82	2.88	2.81	2.84
As_2O_5	0.76	0.76	0.73	0.66
V_2O_3	17.16	17.09	17.11	17.17
WO_3	57.20	57.11	57.15	56.89
H_2O	14.47	14.38	14.36	14.24
	100.00	99.80	99.68	99.38

AMMONIUM PHOSPHO-ARSENO-VANADIO-VANADICO-TUNGSTATE,

$99(NH_4)_2O.12P_2O_5.2As_2O_5.66V_2O_5.6V_2O_3.191WO_3 + 522H_2O.$

Preparation.—From the previous salts produced, it seemed possible to introduce vanadium in two conditions together with the phosphorus and arsenic.

To accomplish this 1 gram of ammonium phosphate, 1 gram of ammonium arsenate, 1 gram of ammonium vanadate, 1 gram of vanadium trioxide, 16 grams of ammonium tungstate, 20 cc. of ammonium hydroxide, and 700 cc. of water were boiled together for six hours. The filtered solution was evaporated, and allowed to stand over night to crystallize.

Properties.—The yield of salt was small. Black octahedral crystals, however, separated. On evaporation of the mother-liquor the crystals, which were minute, were mixed with a large amount of other salts, from which it was difficult to separate them.

The deposit of ammonium chloride, as well as other impurities, were removed to some extent by washing with cold water, in which the crystals themselves were not very soluble. Strong hydrochloric acid decomposed the salt, liberating chlorine and giving a deposit of the hydrated oxide. Strong nitric acid gave a precipitate, soluble on addition of water. Many of the heavy metals produced precipitates that remained insoluble on boiling, but dissolved on addition of a few drops of nitric acid.

RESULT OF ANALYSIS.

	Theory.	Found.		
$(NH_4)_2O$	6.76	6.74	6.74	6.70
P_2O_5	2.21	2.54	2.37	2.41
As_2O_5	0.62	0.61	0.62	0.65
V_2O_5	16.28	16.18	16.18	16.32
V_2O_3	1.22	1.43	1.29	1.28
WO_3	60.06	59.79	59.81	59.79
H_2O.....	12.85	12.73	12.46	12.63
	100.00	100.02	99.47	99.78

There now remained only two more possibilities in these combinations:

Ammonium phospho-arsenico-vanadico-tungstate, and
Ammonium phosphorico-arsenico-vanadico-tungstate.

They were prepared, but the crystals obtained were not well

defined, being also mixed with many impurities. After several attempts to get them, the work was given up. It seems very probable, however, that they can be obtained pure, and will be a subject for further study.

CONCLUSION.

The formulas as given above cannot be looked upon as being definite. The writer is well aware that other views and interpretations may be given to his results, but as even these cannot be absolutely demonstrated, he regards the written formulas as wholly tentative. They will receive further study. They may be multiples of the same, or perhaps not so complicated as would appear. As there is no method, at present, to determine the molecular magnitude of such bodies, the only recourse was the result of analysis. It will be readily seen, that a slight error in the percentage of arsenic or phosphorus would alter the whole formula. It can only be claimed that such compounds exist, and that the constitution assigned to them remains open to correction.

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NOTES.

Additional Note on Filtration of Crude Fiber.—The method of filtering crude fiber described by Mr. Thatcher in the December Journal is one which, I believe, is practiced in a number of laboratories in this country. There is, however, one serious objection to this process. It frequently happens that it is desirable to make a chemical examination of the crude fiber and in such cases the method described by Mr. Thatcher would not answer at all, owing to the contamination of the material with asbestos.

A method eliminating all these difficulties is found in the use of a Büchner funnel, using well-fitting filters of hardened paper. These filters are perfectly resistant to the boiling acid and alkaline solutions. In the König method it is advisable to dilute the boiling glycerol-sulphuric acid with an equal volume of hot water before filtering. Using suction, the filtration is very rapid, owing to the large surface exposed. After washing the fiber with hot water, it is treated with a little alcohol and, after sucking as dry as possible, scraped or brushed from the paper into a weighing-

bottle, where it is dried and weighed. The fiber obtained in this way is in excellent condition for further examination (microscopic, ash, pentosans, cellulose, etc.). There is no danger of contamination with fiber from the hardened filters; in fact the latter may be re-used many times. C. A. BROWNE, JR.

NEW BOOKS.

NOTIONS FONDAMENTALES DE CHEMIE ORGANIQUE. PAR CH. MOUREAU, Professor agrégé a l'École superieure de Pharmacie de l'Université de Paris. Paris: Gauthier-Villars. 1902. 286 pp.

This book may be useful under French conditions as a syllabus or memorandum in connection with a course of lectures on theoretical organic chemistry to mature students, but it is difficult to see in what way it can serve American teachers or American elementary students.

The book is clearly written but has grave faults in the selection and arrangement of material for a book intended for beginners. Its preface indicates that it is an introduction to organic chemistry. But elementary students could hardly avoid being overwhelmed by the first 60 pages which are devoted to an outline of theory which includes atoms, molecules, isomerism, valence, radicals, bonding, saturation and unsaturation, homology, nomenclature and the stereochemistry of carbon, nitrogen, and sulphur; and all this before a substance is described or its mode of occurrence or preparation are indicated. In a book of reference and if accompanied by original references, this outline would be admirable but in this place it seems excessive.

In the body of the book, substances are treated together which contain the same substituted radical, which have the same kind of functional activity. The treatment is clear and the classification has its advantages but it is questionable whether in an elementary book it is not better to take up first methane and its homologues and their derivatives, each class of which is made up of members so nearly alike that a full study of one is a nearly complete study of all, and then turn to the other hydrocarbons to study them and their derivatives by illustration and in the mass.

The absence, in the majority of cases, of any statement of the sources of substances which are found in nature is quite noticeable especially in a book written by a professor in a school of phar-

macy and so also is the absence of any indications of the industrial value of substances. It would have been more logical either to include more such material or else to omit the small amount now included.

It is perhaps hardly necessary to mention that the book has no alphabetical index, a time-saving device which seems to be appreciated by very few French writers. H. W. HILLYER.

AN INTRODUCTION TO CHEMISTRY. By D. S. MACNAIR. London: George Bell & Sons. 1902. xii + 187 pp.

This is an admirable example of that class of text-books to which Professor Alexander Smith refers in his "Teaching of Chemistry in the Secondary School" under the heading of "The Nature Study Method." No reference is made to the atomic theory, but formulae and equations are freely used, being treated "solely as a short-hand expression of the proportions by weight in which the elements are found by experiment to combine." All but a few of the experiments (intended to be performed by the teacher) are within the capabilities of boys of fourteen or fifteen.

A. M. PATTERSON.

CHEMISTRY BY OBSERVATION, EXPERIMENT AND INDUCTION. A LABORATORY MANUAL FOR STUDENTS. By J. I. D. HINDS, PH.D., Professor of Chemistry in the University of Nashville. New York: John Wiley & Sons. 1902. 12mo., viii + 192 pp. Price, 75 cents.

This laboratory manual is divided into four parts: In the first part, consisting of 25 pages, there is a description of the commoner forms of laboratory appliances and some instruction in manipulation. The second part, 9 pages, contains instructions and questions on specific gravity, electrolysis, specific heat and the reduction of gas volumes to normal conditions. The third part, 8 pages, entitled "theoretical chemistry" deals with chemical and physical changes, elements and compounds, acids, bases and salts. The fourth part, 144 pages, is devoted to descriptive chemistry. The elements and compounds are prepared according to the directions given and the student's attention is called to the salient properties of the substances he has made by a number of questions. The book serves also as a laboratory note-book, as sufficient space is left in the text for the written answers to the questions. In the opinion of the reviewer the book would have been improved by the introduction of some accurate quantitative experiments illustrating some of the general laws of chemical combination. Also an

elementary exposition of the theories of solution, ionization, etc., would not have been out of place. EDWARD H. KEISER.

A TEXT-BOOK OF QUANTITATIVE CHEMICAL ANALYSIS. BY FRANK JULIAN. St. Paul, Minn.: The Ramsey Publishing Co. 1902. 604 pp. Price, $6.00 net.

"This volume is intended for the aid of students who, having a fair acquaintance with the elements of general chemistry, can devote a limited time to quantitative analysis concurrent with or following the usual qualitative course; and as an introduction to the monographs on special departments of technical analysis....."

"In Part I, after outlining the general principles of the art, there are described the operations of solution, precipitation, etc., and the appliances commonly employed for the purposes." In Part II is found "a graded series of exercises chosen with a view to illustrate the leading principles in analysis....." In Part III technical analysis and special methods are considered. Part IV contains "Notes on the Methods of Analysis," while an appendix offers a discussion of "certain phases of the important subject of the practice of technical and industrial analysis."

This brief summary may serve, perhaps, to give an idea of the scope of the book. It seems hardly probable that it will be serviceable to students, who "can devote only a limited time to quantitative analysis," nor to "those who are content to remain permanently at routine analysis," but to young men who wish to become chemists, to more advanced students, who are anxious to broaden their horizon, and to the technical chemists, who have regard for something beyond their daily duties, it can not fail to be helpful.

Although it lacks, necessarily, the detail of special monographs or of extended works like those of Boeckman, Allen, and others, there is scarcely a similar book of moderate size, in which so many valuable suggestions can be found.

Among the topics treated with exceptional fulness are the following: Attributive Methods, Calculation of Analyses, Errors and Precautions, Colorimetry, Proximate Organic Analysis, Notes on the Methods of Analysis.

One may question the usefulness of this book as a laboratory guide, another may prefer a different selection of exercises for the illustration of the principles of analysis; others may hold opinions

contrary to those of the author, but none, I think, will fail to find it abounding in information, stimulating and tending to the advancement of the science and art of analysis. L. B. HALL.

QUANTITATIVE CLASSIFICATION OF IGNEOUS ROCKS, BASED ON CHEMICAL AND MINERAL CHARACTERS. BY WHITMAN CROSS, JOSEPH P. IDDINGS, LOUIS V. PIRSSON, HENRY S. WASHINGTON. With an Introductory Review of the Development of Systematic Petrography in the Nineteenth Century, by WHITMAN CROSS. Chicago: The University of Chicago Press. London: William Wesley & Son. 1903. 283 pp.

In this volume have been brought together the two essays under the above titles that appeared in Volume X of the *Journal of Geology* (see abstracts in this Journal, **24**, R., 454, and **25**, R., 7), with the addition of tables to aid in the calculation of the mineral and chemical compositions of rocks, and with a glossary of the new terms employed in the nomenclature. To adequately review this important work would require much space. It seems, therefore, only necessary to refer to the second of the above-mentioned abstracts, and to quote the following passages from the authors' preface.

"Much of the material will be useful to those, also, who do not follow the new classification, since it has a general application to petrography. Thus the 'Review of the Development of Systematic Petrography in the Nineteenth Century' presents a historical sketch of the subject which is valuable to all students of petrology."

"The methods of calculation by which the minerals of a rock may be reckoned from its chemical analysis, and the reverse process, will become more and more of a requirement in the practice of petrographers, as the demand for quantitative description increases. And the convenience of tables in carrying on the operation will be appreciated by all who undertake the work."

"The glossary will be found useful to those who adopt the new system in defining specifically each new term, particularly the magmatic names which appear for the most part only in the tables of the five classes where it requires some consideration to frame their definitions. Their full value will be appreciated when they are studied in connection with the collection of some thousands of rock analyses made within the past fifteen years, which has been prepared by Henry S. Washington, and will be published shortly."

"It is hoped that the present publication will contribute to the

better understanding of the development of petrography, and to a fuller appreciation of its defects and needs, and will point out a way along which substantial advancement may be made in the future."

W. F. HILLEBRAND.

ŒUVRES COMPLÈTES DE J.-C. GALISSARD DE MARIGNAC Tome I 1840–1860 Paris: Masson et Compagnie. Price, by subscription, 25 francs for the two volumes.

This is a beautiful volume of $8 + lv + 701$ quarto pages. Fifty-five pages contain a well-balanced and admirable account of the life and scientific labors of the great Swiss chemist, written with affectionate and well-controlled enthusiasm by his son-in-law. Then follow the earlier half of his scientific papers, which appeared before the end of the year 1860. Thirty-eight are memoirs reporting his own work, and twelve are notes commenting on papers of other scientific men which were closely related to subjects treated in his own papers. The order is chronological, and the paging of the original memoirs is reproduced in the margin.

Marignac was born in Geneva in 1817, and was professor of chemistry there from 1841, as well as of mineralogy also from 1845, till failing health put an end to his teaching in 1878. For perhaps five years longer, he was able to accomplish something in a private laboratory at his house; afterwards, till his death in 1894, he retained his full intellectual powers, and endured with fortitude a good deal of suffering.

Four of his papers were undertaken under the direction of Liebig, and belong to organic chemistry. A few relate to mineralogy; Marignac enjoyed pedestrian tours among the Alps, from which he brought back minerals which he loved to investigate. One paper concerns the theory of the famous experiment of Foucault in which the rotation of the earth is demonstrated by the change of the plane of motion of a free pendulum. One concerns the properties of sulphuric acid, and one describes a hydraulic blowing engine used in Westphalia; Marignac was *Ingenieur des Mines.*

The remaining papers of the present volume are all the work of a great chemist of splendid manipulative skill who devoted the best efforts of his life to the determination of atomic weights. Many were the elements for which his results will always be an

important part of our material. He gave values for no less than twenty-eight elements besides gadolinium, and also accomplished much crystallographic work, suggested by Mitscherlich's law of isomorphism, and bearing upon the formulae of compounds of silicic, titanic, tungstic and other acids. The determination of the atomic weights of cerium, lanthanum, didymium, and other elements, led to studies of the rare earths. A considerable labor on the specific heats of solutions of certain salts was also suggested by his interest in atomic weights. The Royal Society's catalogue makes us eager to see the papers remaining for the second volume, now about due.

It is much to be desired that this impressive record of the great work of an eminent chemist be made easily accessible in the United States. EDWARD W. MORLEY.

A LABORATORY OUTLINE OF GENERAL CHEMISTRY. BY ALEXANDER SMITH, B.SC., PH.D., Associate Professor of Chemistry in the University of Chicago. Second edition, revised.

The reviewer has read this laboratory guide with interest and pleasure. It has appealed to him as a teacher, who has followed practically similar methods in the instruction of beginners for many years, and naturally the process of development and the examples in experimentation have proved very attractive. It is scarcely to be expected that exceptions would not be found to the array of experiments and the modes of procedure—every teacher will make some exceptions, for each one has his own favorite solution of the problems confronting him, as has Dr. Smith; otherwise this little volume probably would not have been prepared in the face of the numerous existing guides upon the same subject. But one doubt shall be mentioned. It is that the exercises here and there seem to call for knowledge and manipulative skill beyond that which the beginner, absolutely ignorant of chemistry, possesses, and upon whose mind the truths deduced will not make the lasting impression for which every teacher so fondly hopes. It strikes one as if the course, pursued as laid down, would be splendidly adapted to students who have some knowledge of the subject and whose purpose it is to obtain a well rounded-out course in general experimental chemistry. Perhaps by the judicious selection of experiments and a final general review, omitting nothing, the main object would be attained. However,

the little volume should be carefully studied. It wi.. help many. It merits recognition and will receive it. It is the product of an earnest, wide-awake and thoughtful teacher who has performed his task with consummate skill—with lucidity in statement, accuracy in fact and care in detail; hence, it is most welcome.

EDGAR F. SMITH.

BIOCHEMISCHES CENTRALBLATT.

The great strides made in medical chemistry and in those fields of medicine verging on chemistry have necessitated the publication of a central organ. This is now published in Berlin by Carl Oppenheimer, under the direction of Ehrlich, Fischer, Kossel, Liebreich, Müller, Proskauer, Salkowski and Zunts, and they have appointed Heinrich Stern, of New York, editor for the United States and Canada. The object of the publication will be:

A—To report such experiments and observations of physical and applied chemistry as are of importance to the physician.

B—Reports on the physiology of plants.

C—Physiological chemistry in the narrower sense (constituents of the body and their derivatives).

D—Chemistry of the tissues and organs under normal and pathological conditions.

E—Chemistry of digestion, secretions and excretions, metabolism and blood.

F—Ferments and fermentation; toxins of a non-bacterial nature.

G—Chemistry of the pathogenic micro-organisms (toxins, anti-toxins), phenomena of immunity.

H—Toxicology and pharmacology.

I—Hygienic chemistry, disinfection, examination of water.

As this is the only international organ devoted to these scientific fields, American observers and investigators will find it to their interests to prepare abstracts of their papers which have appeared since January 1st and will appear hereafter, and send them to Heinrich Stern, 56 East 76th Street, New York City.